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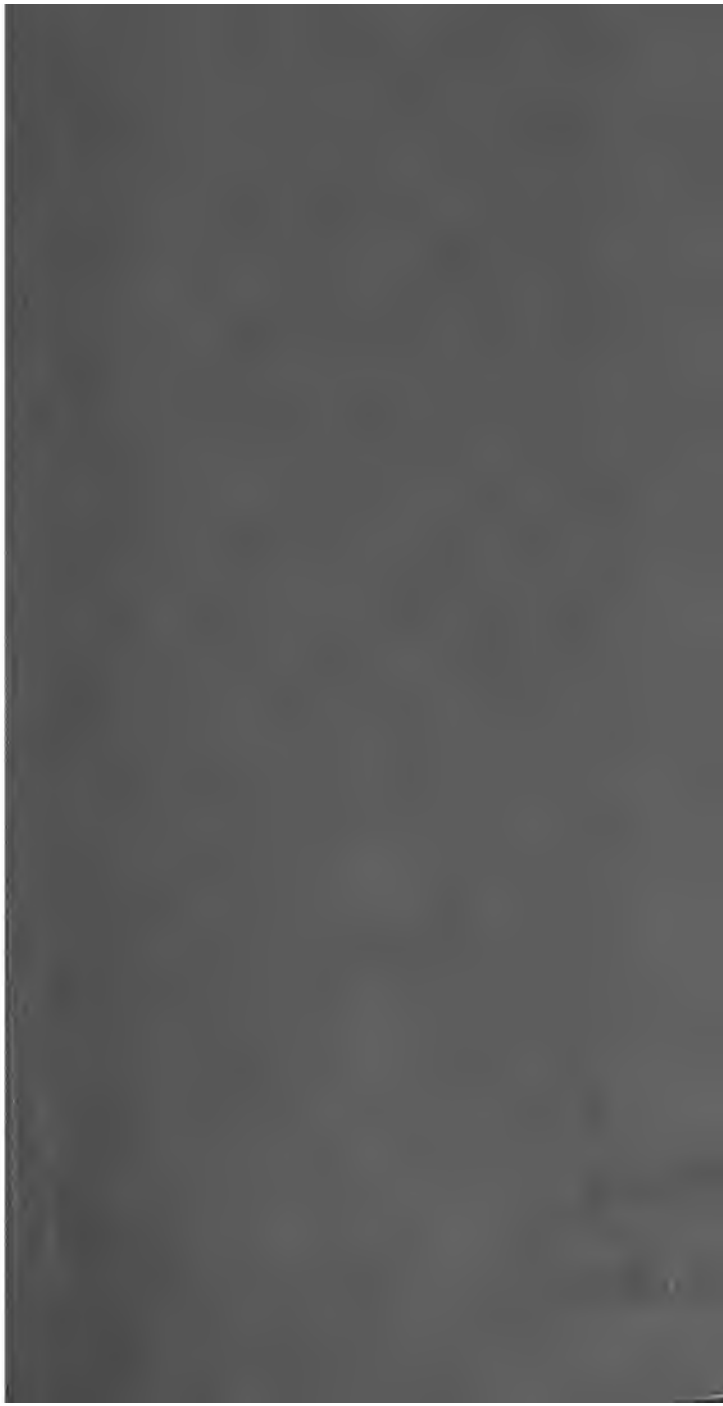

SELECT METHODS

IN

QUANTITATIVE ANALYSIS

BY

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PARTS I AND II.

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PART I.

ERRATA.

Page 8, third line, *weight* should read *weigh.*

Page 33, eleventh line, *diliquescent* should read *deliquescent; Bottle 12* should read *Box 12.*

Page 35, second paragraph, *page 10* should read *page 14.*

Page 39, second paragraph, *page 21* should read *page 24.*

Page 49, paragraph (*e*), *page 20* should read *page 28.*

Page 59, fifth paragraph, *page 60* should read *page 66;* first footnote should read *Fresenius 439.*

Page 61, first paragraph, *page 52* should read *page 60;* second paragraph, *page 70* should read *page 76.*

Page 63, second paragraph, *page 47* should read *page 57.*

REFERENCES.

FRESENIUS: *Quant. Anal.;* 7th Ed.

CLASSEN.

CROOKES: *Select Methods;* 2d Ed.

WATTS' *Dictionary.*

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HART: *Volumet. Anal.*

Chemical News.

LIST OF ELEMENTS.*

Hydrogen = 1.

Name.	Symbol.	Atomic Weight.	Atomic Weight Adopted in this Edition.
Aluminium	Al	27.04	27.04
Antimony	Sb	119.6	119.6
Arsenic	As	74.9	75.0
Barium	Ba	136.86	136.9
Bismuth	Bi	207.5	207.5
Bromine	Br	79.76	79.8
Boron	B	10.9	11.0
Cadmium	Cd	111.7	111.7
Calcium	Ca	39.91	40.0
Carbon	C	11.97	12.0
Cerium	Ce	141.2	141.2
Chlorine	Cl	35.37	35.37
Chromium	Cr	52.45	52.45
Cobalt	Co	58.6	58.6
Copper	Cu	63.18	63.18
Fluorine	F	19.06	19.06
Gold	Au	196.2	196.2
Hydrogen	H	1.	1.0
Iodine	I	126.5	126.5
Iron	Fe	55.88	56.0
Lead	Pb	206.39	206.4
Lithium	Li	7.01	7.01
Magnesium	Mg	23.94	24.0
Manganese	Mn	54.8	55.0
Mercury	Hg	199.8	199.8
Molybdenum	Mo	95.9	96.0
Nickel	Ni	58.6	58.6
Nitrogen	N	14.01	14.0
Oxygen	O	15.96	16.0
Platinum	Pt	194.3	194.3
Phosphorus	P	30.96	31.0
Potassium	K	39.03	39.0
Silver	Ag	107.66	107.66
Silicon	Si	28.0	28.0
Sodium	Na	22.99	23.0
Strontium	Sr	87.3	87.3
Sulphur	S	31.98	32.0
Tin	Sn	117.35	117.35
Titanium	Ti	50.25	50.25
Tungsten	W	183.6	183.6
Uranium	Ur	239.8	240.0
Zinc	Zn	64.88	65.0

* Meyer Atomgewichte.

RULES FOR WEIGHING.

1. Level and adjust the balance.

2. Always place the substance to be weighed upon the same pan—most conveniently upon the left.

3. Never place the substance upon the naked pan; use counterpoised watch-glasses, or a weighed porcelain or platinum dish. (Never use paper).

4. Always bring the balance to a rest, before placing upon or removing a substance or weight from the pans.

5. Use forceps, if possible, in placing upon and removing dishes from the pans.

6. Always handle weights with forceps; never touch them with the hand.

7. Never weigh a vessel or substance while warm.

8. Never try weights at random; commence with the weight nearest to, and less than the substance, and add the weight next in succession till the correct weight is obtained.

9. Liquids, and solids which are volatile, or give off or absorb moisture when exposed to the air, must be weighed in closed vessels. All other substances may be weighed in the open air.

SPECIFIC GRAVITY.*

The specific gravity of a body is the weight of that body as compared with the weight of an equal volume of a standard body, which is taken as unity. In all cases of solids and liquids, this standard of unity is pure water at 60° F. = 15.5° C.

Water being taken as unity, or one, any other substance will be more or less than one. The results are expressed in whole numbers and decimals; the decimals are carried to the third place.

Water = 1.000 (one, not one thousand).
Alcohol = 0.815
Sand = 2.127

Gravimetric Methods of Determining the Specific Gravities of Solids and Liquids.

The following classification will serve for all solids and liquids which are likely to occur in ordinary investigations.

1. Liquids, heavier or lighter than water.
2. Solids, in powder, heavier than water and insoluble in it.
3. Solids, in mass, heavier than water and insoluble in it.
4. Solids, lighter than water and insoluble in it.
5. Solids, soluble in water.

CLASS I.—*Liquids, heavier or lighter than water.*

Take a specific gravity bottle, clean and dry it; cool and weigh.

---

* Watts Dict' V—857.

Now fill the bottle with distilled water at 60° F., (there must not be any air bubbles about the stopper) and again weight it.

It will not be necessary to repeat these weighings except in cases of accident.

Empty and dry bottle, cool and fill with *the liquid* at 60° F., (avoiding air bubbles as before) and weigh.

We thus obtain the weight of an equal volume of pure water and liquid thus:

Let B = sp. gr. bottle, W = distilled water, and L = the liquid.

B + W	= 30 grms.	B + L	= 38 grms.
B	= 10 grms.	B	= 10 grms.
W	= 20 grms.	L	= 28 grms.

To find the sp. gr. of the liquid, divide the weight of the liquid by the weight of pure water.

$$\frac{L}{W} = \frac{28}{20} = 1.400 \text{ sp. gr. of the liquid;}$$

or, placing it in the form of a proportion,

$$20 : 28 : : 1.000 : x, = \text{sp. gr.}$$

Determine the sp. gr. of the following table reagents:
HCl—HNO_3—$H(C_2H_3O_2)$—KHO—NH_4HO—C_2H_6O.

CLASS II.—*Solids, in powder, heavier than water and insoluble in it.*

(*Boxes 1 and 2.*)

Clean and dry the specific gravity bottle, cool and put into it from 2 to 5 grms. of the powder and weigh. Then fill the bottle with distilled water (avoiding air bubbles) and weigh. Result:

B + W	= 30 grms.	B + S	= 20 grms.
B	= 10 grms.	B	= 10 grms.
W	= 20 grms.	S	= 10 grms.
B + S + W	= 36 grm.	W	= 20
B + S	= 20 "	W^1	= 16.
W^1	= 16 "	W^{11}	= 4.

W = the weight of water which the bottle holds.
W^1 = " " " above the substance.
W^{11} = " " " displaced by the substance.

Displaced water has the same volume as the substance which displaced it; and since we have the weight of the substance, and the weight of the water displaced by it, we therefore have the weight of an equal volume of both.

Applying the rule just given, we have

$$\frac{S}{W^{11}} = \frac{10}{4} = 2.500 \text{ the sp. gr. of S.}$$

CLASS III.—*Solids, in mass, heavier than water and insoluble in it.*

(*Box 3.*)

Suspend the substance from the arm of the balance by means of a horse-hair, and then weigh. Now place a beaker of distilled water in such a position that the substance hangs freely in it, and again weigh, (see that no air bubbles adhere to the substance).

The loss in weight is equal to that of the water displaced. Thus

S in air = 25 grms.
" water = 15 "
Loss = 10 "

which is the weight of the displaced water, = W

$$\frac{S}{W} = \frac{25}{10} = 2.500 \text{ sp. gr. of S.}$$

CLASS IV.—*Solids lighter than water and insoluble in it.*

(*Boxes 4 and 5.*)

These being lighter than water, will not sink in it; therefore some heavy substance must be attached to them, to sink them, and thus displace the water.

Take as an example, wood:

1. Weight of sinker in air = 50.
2. " " " + wood " = 183.

wood " = 133.

3. Weight of sinker + wood in water = 38.
4. " " " in water = 44.

2wt.— 3wt. / 183 — 38 = 145 } Weight of the water displaced by sinker and wood. } = W^{I}.

1wt.— 4wt. / 50 — 44 = 6 } Weight of the water displaced by sinker. } = W^{II}.

$W^{I} - W^{II}$ / 145 — 6 = 139 } Weight of the water displaced by wood. } = W^{III}.

$$\frac{\text{Wood}}{W^{III}} = \frac{133}{139} = 0.956 \text{ sp. gr. of wood.}$$

CLASS V.—*Solids soluble in water.*

(*Box 6.*)

Select some liquid in which the solid is insoluble, and determine its sp. gr.

Then proceed to determine the sp. gr. of the solid according to directions given for Class Two, using this liquid instead of water.

(The substance in Box 6 is insoluble in alcohol.)

Multiply the sp. gr. thus obtained by the sp. gr. of the liquid used; the product will be the true sp. gr.

QUANTITATIVE ANALYSIS.

PRELIMINARY STEPS.

1. *Selecting the Sample.*—The mode of selecting the sample will depend upon the object sought. In commercial work the sample should be so selected as to represent as nearly as possible the average quality of the whole. This can be best accomplished by pulverizing a large quantity, taken from different parts of the mass, thoroughly mixing the same and then taking from this a small sample for analysis.

In technical work, pure, clean crystals should be selected.

2. *Mechanical Division.*—Substances soluble in water or readily soluble in acids, are only pulverized moderately fine; they must be fine enough, however, to insure a uniform sample. A porcelain mortar answers for this work. Substances not readily dissolved by acids, or soluble only after fusion, must be reduced to an impalpable powder with an agate mortar.

3. *Drying the Sample.*—The sample, when ready for analysis, must be in a definite state, that is, in a condition in which it can always be obtained a second time, if by accident or otherwise a new sample has to be prepared. This is accomplished by drying, which removes the hygroscopic moisture. The mode of drying will depend upon certain physical characteristics peculiar to different bodies.

Classification of Substances, with reference to the mode of drying.

(*a*). Substances which lose water of constitution or crystallization when exposed to air are dried by pressing between folds of blotting paper.

(*b*). Substances which only give off water in artificially dried air, are pressed between folds of blotting paper and then left for some time exposed to the air, protected from dust by paper or otherwise.

(*c*). Substances which undergo no change in dry air, but lose water at 100° C., are dried in a desiccator over H_2SO_4 or $CaCl_2$.

(*d*). Substances which give off all their moisture at 100° C., but undergo no other change, are dried in a water bath at 100° C.

(*e*). Some substances retain moisture at 100° C., this moisture is generally determined and returned as per cent.

GRAVIMETRIC DETERMINATIONS.

The crucible which is used for igniting and weighing the precipitate must be cleaned, heated, cooled in the desiccator, and weighed before each ignition.

The ash of the filter must also be determined by incinerating two or more filters till white, and weighing the resulting ash.

Box 1.

BARIUM CHLORIDE.

Estimation of Barium.—Take an exact weight (about 0.5 grm.*) of the substance, dissolve in 100 c. c. of water, acidulate with HCl, boil and add, drop by drop, dilute H_2SO_4 as long as a precipitate forms; boil for some time, then place to one side until the precipitate has completely subsided; filter by decantation and wash with hot water, until silver nitrate produces no turbidity in the washings.

Dry, ignite, cool, add a few drops of H_2SO_4, ignite moderately till fumes are no longer given off, cool and weigh.

Result, $BaSO_4$.

Calculation.

$BaSO_4$: Ba : : wt. $BaSO_4$: x = wt. of Ba found.
Wt. taken : x : : 100 : y = per cent. of Ba.

Estimation of Chlorine.—Dissolve 0.2 grms. in 50 c. c. of warm water, add silver nitrate in slight excess, then acidify with HNO_3, heat and agitate briskly; place the beaker for a short time in a warm, dark place, then filter

*The beginner should never weigh 1. grm. or .5 grm., but take a quantity, near the amount specified, and weigh it carefully. Sometimes a definite amount will be specified, when from the context it will be evident that an approximate quantity is intended.

and wash with hot water. Wash till filtrate gives no precipitate on adding HCl.

Dry, remove the precipitate from the filter, incinerate the filter, then add the precipitate to the ash, cool, add 5 drops of HNO_3, heat gently, then add 10 drops HCl, heat on water bath till dry, then ignite until the AgCl begins to fuse.

Result = AgCl.

Calculation.

AgCl : Cl : : wt. AgCl : x = Cl in wt. taken.
Wt. taken : x : : 100 : y = per cent. of Cl.

To remove the fused AgCl from the crucible, place upon it a piece of Zn and add dilute H_2SO_4.

Box 2.

MAGNESIUM SULPHATE.

Estimation of Magnesium Oxide.—Dissolve 0.5 grm. in 50 c. c. of water, add NH_4Cl, then NH_4OH in excess (no precipitate should be formed; if there is, add HCl till dissolved; then add NH_4OH in excess); cool, and add sodium-ammonium phosphate in slight excess; agitate briskly, allow to stand till the supernatant liquid is clear; filter and wash the precipitate with a mixture of one part ammonium hydrate and three parts water, until the addition of HNO_3 and $AgNO_3$ to the filtrate does not produce a precipitate. Dry and ignite (commencing with a low heat) until constant weight is obtained.

If, after ignition, the precipitate is not pure white, moisten it with nitric acid, and again ignite.

Result = $Mg_2P_2O_7$.

Calculation.

$Mg_2P_2O_7$: 2MgO : : wt. $Mg_2P_2O_7$: x = MgO in wt. taken.
Wt. taken : x : : 100 : y = per cent. of MgO.

Estimation of Sulphuric Acid.—Dissolve 0.5 grm. in 30 c. c. of water, acidulate with HCl, boil and add to it a

boiling solution of Barium chloride, as long as a precipitate is formed; (now proceed as directed under Box 1 for the estimation of Barium.)

Box 3.

FERROUS SULPHATE.

Estimation of Metallic Iron.—Dissolve 1 grm. in 25 c. c. of water strongly acidulated with HCl, boil, and add small crystals of $KClO_3$, until all the iron is oxidized to the ferric salt; continue the boiling and add more HCl if necessary, until the $KClO_3$ is decomposed and the solution no longer emits an odor of chlorine; cool and add NH_4OH in excess; boil, filter by decantation and wash with hot water, until silver nitrate produces no turbidity in the washings when acidulated with HNO_3.

Dry, ignite and weigh.

Result = Fe_2O_3.

Calculation.

$Fe_2O_3 : 2Fe : :$ wt. $Fe_2O_3 : x =$ Fe in wt. taken.

Wt. taken $: x : : 100 : y =$ per cent. of Fe.

Box 4.

CALCIUM CARBONATE.

Estimation of Calcium Oxide.—Take 0.5 grm., place in a large beaker, add 30 c. c. of water, cover with a clock-glass, then add gradually HCl, till effervescence ceases, heat, add ammonium oxalate in moderate excess, and then ammonia in slight excess, boil, remove to a warm place, and let stand twelve hours; filter by decantation and wash with hot water, until the wash water, acidulated with nitric acid, gives no precipitate with silver nitrate.

Dry, ignite at a moderate heat, cool, moisten with ammonium carbonate, heat to faint redness, cool and weigh; repeat this operation until constant weight is obtained.

Result = $CaCO_3$.

Calculation.

$CaCO_3 : CaO : :$ wt. $CaCO_3 : x = CaO$ in wt. taken.

Wt. taken : $x : : 100 : y =$ per cent. of CaO.

Estimation of Carbon Dioxide.—When CO_2 is combined with a base, it is generally determined by loss of weight which the substance sustains, when treated with a stronger acid or acid compound. The more common method is to employ some simple apparatus which will permit the expulsion of the CO_2, without loss from other causes. The apparatus is charged with a weighed quantity of the substance containing the CO_2, and with the acid which is to expel it, it is then weighed, and after weighing, the acid is allowed to come in contact with the substance, when the CO_2 is expelled, the apparatus is weighed again; the loss in weight is the weight of CO_2.

Wt. taken : loss : : 100 : $x =$ per cent. of CO_2.

Box 5.

SODIUM PHOSPHATE.

Estimation of Phosphoric Acid.—Dissolve 0.5 grm. in 50 c. c. of water, add NH_4OH in excess, cool, then add magnesia mixture in excess, agitate briskly; after standing three hours in a cool place, filter, and wash with a mixture of one part NH_4OH, and three parts water, until the wash water acidulated with HNO_3, gives no precipitate with $AgNO_3$.

(The precipitate is slightly soluble in dilute ammonia water).

Dry, and ignite. (For precautions see Box 2).

Result $= Mg_2P_2O_7$.

Calculation.

$Mg_2P_2O_7 : P_2O_5 : :$ wt. $Mg_2P_2O_7 : x = P_2O_5$ in wt. taken.

Wt. taken : $x : : 100 : y =$ per cent. of P_2O_5.

Box 6.

ARSENIOUS ANHYDRIDE.

Estimation of Arsenic.—Dissolve 0.5 grm. in KHO, with the aid of heat; acidulate with HCl, maintain the heat at 70° C., and pass H_2S gas through the solution for one hour, filter and wash with hot water. If As_2S_3 adheres to the tube and beaker, dissolve it in NH_4OH and reprecipitate with dilute HCl, and transfer it to the filter. Dissolve the moist precipitate on the filter with *cold* NH_4OH, to this ammoniacal solution add *cold* dilute HCl until the solution is moderately acid, filter through counterpoised filters, and wash with water. Dry at 100° C., cool and weigh.

Result = As_2S_3.

Calculation.

$As_2S_3 : As_2 : :$ wt. $As_2S_3 : x =$ As in wt. taken.
Wt. taken $: x : : 100 : y =$ per cent. of As.

VOLUMETRIC ANALYSIS.

Volumetric analysis is a method for determining quantity by measure. The reagent and the material under examination must therefore be in solution.

The reagents which must have an exact and known strength are called *Standard Solutions.*

These are divided into 1. EMPIRICAL. 2. NORMAL.

Empirical Solutions, are used for estimating one element only. They are prepared without reference to the atomic weights, and are generally of such strength, that 1 c. c. = 1 per cent. or the fraction of a per cent. when titrating a given weight of the unknown.

Normal Solutions, are used for estimating all elements, with which they produce a distinct reaction. They are prepared so that a given measure contains an exact atomic weight.

Normal Solutions, are prepared so that one litre at 16° C, shall contain the hydrogen equivalent of the active reagent weighed in grms. (H = 1). If the substance is univalent the full atomic weight is used, if bivalent one-half, and if trivalent one-third. This rule does not hold good in all cases, and the whole, or, an aliquot part of the atomic weight of the reagent must be taken, depending upon its peculiar reaction in any given analysis.

Solutions of less strength than the normal will often be required. These solutions may be shortly designated as N normal; $\frac{N}{2}$ seminormal; $\frac{N}{5}$ quintinormal; $\frac{N}{10}$ decinormal; $\frac{N}{100}$ centinormal.

Titrate, is the term applied to the method of estimating quantitatively the amount of pure substance contained in a given substance or solution, by a standard or titrated solution.

End reaction, is the term applied to that point in the

operation where no further change takes place between the known and the unknown. The end reaction must be manifest to the eye, either by some change in the solution itself, or by an indicator. Reagents which produce no visible change, cannot be used to prepare standard solutions.

Normal factor, is used to express the amount in grms of the active reagent in 1 c. c. of a normal solution.

CLASSIFICATION OF METHODS.

(1). Analysis by saturation, or acidimetry and alkalimetry.

(2). Analysis by oxidation and reduction.

(3). Analysis by precipitation.

Alkalimetry and Acidimetry—or the methods for estimating the per cent. of actual alkali or acid in a given solid or solution.

The end reaction in these determinations is not manifested by the solution itself, hence an indicator must be used.

INDICATORS.

Phenolphthalein—is a yellowish powder, soluble in alcohol. To prepare a solution for use dissolve .010 grm. in 10 c. c. of 50 per cent. alcohol. One or two drops is sufficient for each titration. Acids produce no change in color, alkalies produce an intense purple-red.

This, though perhaps not the best indicator, has been found to work well in the hands of beginners, on account of its great sensitiveness.

It cannot be used for titrating ammonia, or the caustic alkalies when ammoniacal salts are present. Cold or only moderately warm solutions must be used in titrating, oxalic, citric, tartaric, acetic and other organic acids, with potassium or sodium hydrate. Hot solutions must be used in titrating alkaline and earthy hydrates, carbonates, and bicarbonates, and sulphides, with mineral acids.

STANDARD SOLUTIONS.

In preparing standard solutions, it is not always possible to obtain the reagent in a definite and permanent form, so that the exact amount required can be weighed or measured out. In such cases the standard is obtained by titrating the reagent with some standard solution, and then calculating the dilution required to bring the reagent to the standard. The volumes of all standard solutions of a given class (as $\frac{N}{10}$) must be equal, that is 1 c. c. of a given $\frac{N}{10}$ solution must exactly neutralize 1 c. c. of an $\frac{N}{10}$ solution of the opposite kind.

In preparing $\frac{N}{10}$ solutions for this part of the work, we will commence with *oxalic acid*, since this acid can be obtained in a definite and permanent form.

$\frac{N}{10}$ OXALIC ACID.

$C_2O_4H_2, 2H_2O = 126 \div 2 = 63$. 6.3 grms. per litre.

Weigh out exactly 6.3 grms of the freshly prepared crystals of oxalic acid, dissolve in water, and dilute to one litre.

Each c. c. contains .0063 grms of the acid; therefore .0063 is the decinormal factor of oxalic acid.

$\frac{N}{10}$ POTASSIUM HYDRATE.

$KHO = 56$. 5.6 grms. per litre.

Take 50 c. c. of the table reagent, and dilute with water to 600 c. c., cool, and titrate with $\frac{N}{10}$ oxalic acid, as follows: Take 5 c. c. of the KHO solution, add 2 drops of the indicator, and run in gradually from a burette $\frac{N}{10}$ oxalic acid, until a drop just disperses the red color. Make at least six titrations and take the average result.

Example for Calculating the Dilution.—Suppose 5 c.c. of the KHO solution required 8 c. c. of the $\frac{N}{10}$ oxalic acid to produce the end reaction, or to neutralize it. The potash solution is therefore the stronger and must be diluted with water, so that 5 c. c. of it will require just 5 c. c. of the $\frac{N}{10}$ oxalic acid to neutralize it; when so diluted, it will

be an $\frac{N}{10}$ solution, for, as we have said, $\frac{N}{10}$ solutions are all equal, and 1 c. c. of any $\frac{N}{10}$ solution can be substituted for 1 c. c. of any other $\frac{N}{10}$ solution of the same nature.

The graduated cylinder has left in it 550 c. c. of the KHO solution; how many c. c. of an $\frac{N}{10}$ solution will it make?

$$5 \text{ c. c.} : 8 \text{ c. c.} : 550 \text{ c. c.} : x = 880 \text{ c. c.}$$

Now add water to the 550 c. c. until it has been raised to 880 c. c., mix thoroughly, and again titrate with the $\frac{N}{10}$ oxalic acid; the solutions should be equal.

Each c. c. contains .0056 grms KHO.

Burettes with glass taps must not be used for measuring caustics.

$\frac{N}{10}$ SULPHURIC ACID.

$H_2SO_4 = 98 \div 2 = 49$. 4.9 grms per litre.

Take 5 c. c. of the table reagent, dilute with 300 c. c. of water in a porcelain dish, transfer to the graduated cylinder, cool, and titrate with $\frac{N}{10}$ KHO solution; see directions for titrating and making an $\frac{N}{10}$ solution of KHO.

Each c. c. contains .0049 grms. H_2SO_4.

$\frac{N}{10}$ NITRIC ACID.

$HNO_3 = 63$. 6.3 grms. per litre.

Take about 5 c. c. of the table reagent, dilute with 200 c. c. of water, and titrate with $\frac{N}{10}$ KHO solution; see direction for H_2SO_4.

Each c. c. contains .0063 grms. HNO_3.

(The HNO_3 must be free from nitrous fumes).

NORMAL OXALIC ACID.

Take 6.3 grms., dissolve in 80 c. c. of water, and dilute to 100 c. c.

NORMAL SODIUM HYDRATE.

Take about 15 grms. NaHO, place it in a porcelain dish, dissolve in 150 c. c. of water, cool, transfer to a graduated cylinder, and titrate with normal oxalic acid.

From the results calculate the dilution necessary to make a normal solution.

NORMAL TARTARIC ACID.

Take about 20 grms. tartaric acid, dissolve in 150 c. c. of water, cool, and titrate with normal sodium hydrate.

Titrations.

All material, whether solid or liquid, which is to be titrated for the per cent. of any given element, must be weighed.

For convenience in weighing, dissolving, or diluting, select a two-ounce, globe-shaped flask, clean, and dry, and then graduate by running into it, water, from a burette till a distinct meniscus is formed in the neck, and an even number of c. c. has been used; mark this point by a label which bears the number of c. c, used.

This we will call the weighing flask.

TITRATION OF HYDROCHLORIC ACID.

HCl = 36.37. $\frac{N}{10}$ factor = .003637.

Take about 5 c. c. of the table reagent, place it in the weighing flask, and weigh; dilute with water.

Mix thoroughly, cool, and dilute to the mark. Fill a glass tap burette with this solution, and a Mohr's burette with $\frac{N}{10}$ KHO.

Run into a small beaker 5 c. c. of the HCl solution, add two drops of the indicator and titrate with the $\frac{N}{10}$ KHO; repeat the titration three or four times and take the average result.

Calculation.

To find the per cent. of HCl.

HCl taken, weighed 5.6 grms. Weighing-flask holds 60 c. c. 20 c. c. of $\frac{N}{10}$ KHO were required to neutralize 5 c. c. of the diluted HCl.

5 c. c HCl : 20 c. c. $\frac{N}{10}$ KHO : : 60 c. c. : x = 240 c. c. $\frac{N}{10}$ KHO.

Therefore 240 c. c. $\frac{N}{10}$ KHO would be required to neu-

tralize 5.6 grms. HCl (that is the 60 c. c.); or by diluting the 60 c. c. with water to 240 c. c. we would have an $\frac{N}{10}$ solution of HCl.

1 c. c, of an $\frac{N}{10}$ HCl contains .003637 grms. HCl, therefore, 1 : .003637 : : 240 : y = 0.87288 grms. HCl in wt. taken.

Wt. taken (5.6 grms.) : 0.87288 : : 100 : z = per cent. of HCl = 15.58.

Volatile liquids, as NH_4OH and HCy must be weighed in well stopped bottles.

The titration of Acetic Acid by a standard caustic alkali is not rigidly exact, for neutral acetates have an alkaline reaction.

Titrate the following table reagents:

HNO_3	$\frac{N}{10}$ factor	= .0063
HCl	" "	= .003637
$C_2O_2H_4$	" "	= .006
KHO	" "	= .0056

Box 1.

CITRIC ACID. $C_6O_7H_8 + H_2O = 210 \div 3 = 70.$

$\frac{N}{10}$ factor = .007

Dissolve about 0.2 grm. in water, in the weighing flask, and dilute to the mark, then titrate with $\frac{N}{10}$ KHO.

Box 2.

SODIUM CARBONATE. Na_2CO_3.

To be titrated for $Na_2O = 62 \div 2 = 31.$

$\frac{N}{10}$ factor of Na_2O = .0031.

Place about 0.5 grm. in the weighing flask, dissolve in water and dilute to the mark.

Take 5 c. c. of this solution in a small beaker, add some water, then add two drops of the indicator, and run in from a burette $\frac{N}{10}$ H_2SO_4, ½ c. c. at a time (boiling after each addition) till the H_2SO_4 is in excess; boil at least five minutes after the last addition of H_2SO_4. Now titrate back the excess of H_2SO_4 with $\frac{N}{10}$ KHO. A drop or two

of the indicator may be required from time to time during the titration.

The difference between the H_2SO_4 and KHO used, is the amount of H_2SO_4 required to neutralize the 5 c. c.

Box 3.

SODIUM BICARBONATE. $NaHCO_3$.

To be titrated for NaHO = 40

$\frac{N}{10}$ factor of NaHO = .004

Follow directions for Box 2.

Box 4.

CALCIUM CARBONATE. $CaCO_3$.

To be titrated for $CO_2 = 44 \div 2 = 22$.

Normal factor for $CO_2 = 0.022$

Take about .05 grm. in a large beaker, add water enough to cover the bottom of the beaker, then titrate according to directions given for Box 2, using normal HNO_3 in place of $\frac{N}{10}$ H_2SO_4.

Bottle 5.

SOLUTION OF CAUSTIC POTASH AND SODA.

(Must not be weaker than a normal solution).

Normal factor of KHO = .056.

Normal factor of NaHO = .04.

Place about 10 grms. in a flask (must not dilute), run in from a burette normal tartaric acid, till neutral or faintly acid, note the number of c. c. used, and then run in just as much more. This will form a bitartrate of potash and soda; cork the flask and shake violently for a few minutes, this will cause the potassium bitartrate to separate almost completely, since it is insoluble in sodium bitartrate. Filter and when the filtrate has all passed through, rinse out the flask with 5 c. c. of water and pour it on the filter; when all has passed through, titrate the filtrate with normal NaHO; the number of c. c. of normal NaHO required, equals the soda in the mixture.

Calculation.

10 grms. of the solution were taken. 5 c. c. of normal NaHO were used; $5 \times .04 = 0.2$ grms. of NaHO in wt. taken.

$$10 : 0.2 : : 100 : x = 2 \text{ per cent. of NaHO.}$$

24 c. c. of normal tartaric acid were used; 24 c. c.—10 c. c. (the amount of tartaric acid in combination with soda as bitartrate) = 14 c. c. the amount of acid in combination with the potash as bitartrate; 14 c. c. $\div$ 2 = 7 c. c., the amount of normal acid required to make a neutral tartrate of the potash.

$$7 \times .056 = .392 \text{ grm. KHO in wt. taken.}$$
$$10 : .392 : : 100 : y = 3{,}92 \text{ per cent. of KHO.}$$

OXIDATION AND REDUCTION.

The most available oxidizing reagents are

$$KMnO_4, \quad K_2Cr_2O_7, \text{ and I.}$$

The most available reducing reagents are

$$FeSO_4, \quad C_2O_4H_2{,}2H_2O, \quad H_2SO_3, \quad Na_2S_2O_3, \quad As_2O_3, \text{ and } SnCl_2.$$

$\frac{N}{10}$ POTASSIUM PERMANGANATE.

$KMnO_4 = 158 \div 5 = 31.6$. 3.16 grms. per litre.

Select some clean crystals, dry them for forty-eight hours in a desiccator over H_2SO_4; then weigh out 3.16 grms., dissolve in water and dilute to one litre. If the salt is pure, the solution will be $\frac{N}{10}$; but as this is not always the case it must be titrated with some reducing reagent which has a definite and constant composition. $\frac{N}{10}$ $KMnO_4$ cannot be used when there is much free HCl present in the solution to be titrated, for free HCl reduces the permanganate.

In preparing standard solutions it is never safe to rely upon a solution made by taking a required weight, for

there may be some impurity in the reagent. The solution should always be compared with one or more solutions of the opposite kind.

TITRATION OF PERMANGANATE.

(*a*) *With* $\frac{N}{10}$ *Ferrous Sulphate.*—Measure with a pipette, 5 c.c. of $\frac{N}{10}$ $FeSO_4$ into a small beaker, add some dilute H_2SO_4 (1 to 5), and titrate with the $\frac{N}{10}$ permanganate, till a faint, permanent permanganate color is produced, (use a glass tap burette).

Reaction.

$$10FeSO_4 + 8H_2SO_4 + 2KMnO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

(*b*) *With* $\frac{N}{10}$ *Oxalic Acid.*—Follow directions given under (*a*); (warm the oxalic acid to 60° C., before titrating).

Reaction.

$$5C_2H_2O_4 + 3H_2SO_4 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2.$$

(*c*) *With* $\frac{N}{10}$ *Sodium Hyposulphite.*—Measure into a flask one ounce of KI—table reagent—(which has no free iodine), add 2 c.c. HCl (1.16), dilute largely with water, then run in 5 c.c., of $\frac{N}{10}$ $KMnO_4$, cork the flask, and shake thoroughly; (must be kept cold), now titrate with $\frac{N}{10}$ sodium hyposulphite, until the solution is colorless, then run in $\frac{N}{10}$ $KMnO_4$, one drop at a time till the iodine color re-appears.

$\frac{N}{10}$ POTASSIUM BICHROMATE.

$K_2Cr_2O_7 = 294.9 \div 6 = 49.15$. 4.915 grms. per litre.

Weigh 4.915 grms. of the pure crystals, dissolve in water, and dilute to one litre.

Bichromate possesses the advantage over permanganate, that it is absolutely permanent in solution, may easily be obtained in a pure state, may be used in a Mohr's burette, and can be used in the presence of free sulphuric or hydrochloric acid. It possesses the disadvantage, in

that, it requires an indicator, and cannot be used in the presence of zinc.

Indicator Required.

Potassium Ferricyanide,—must be freshly prepared, and so dilute, that when a drop is placed on a marble slab it shows but a faint color.

TITRATION OF BICHROMATE.

(*a*) *With* $\frac{N}{10}$ *Ferrous Sulphate.*—Measure, with a pipette, 5 c. c. of $\frac{N}{10}$ $FeSO_4$, into a beaker, add some dilute H_2SO_4 and run in $\frac{N}{10}$ $K_2Cr_2O_7$, till a drop, brought in contact with a drop of the indicator on a marble or porcelain slab fails to give a blue color.

Reaction.

$$6FeSO_4 + 7H_2SO_4 + K_2Cr_2O_7 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

(*b*) *With* $\frac{N}{10}$ *Sodium Hyposulphite*—according to directions given under titration of permanganate (*c*).

$\frac{N}{10}$ IODINE.

Iodine = 126.5. 12.65 grms. per litre.

Place in a glass stoppered bottle about three grms. and weigh. (The bottle must be kept closed while weighing to prevent the iodine, which is very volatile, from injuring the balance). Prepare a solution of KI by taking ten grms. and dissolving it in 100 c. c. of water; transfer the iodine to the graduated cylinder, rinsing the weighing bottle with this solution; shake the cylinder till the iodine is dissolved.

To calculate the dilution.

12.65 : 1000 : : wt. taken : x. x = dilution.

This solution changes after standing some time, and must therefore be often tested.

TITRATION OF IODINE.

(*a*) *With* $\frac{N}{10}$ *Sodium Hyposulphite.*—Take 5 c. c. of $\frac{N}{10}$

sodium hyposulphite, add a few drops of starch indicator, and run in the iodine solution till one drop produces a permanent blue color. (The solution must not be heated).

Reaction.

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6.$$

(*c*) *With* $\frac{N}{10}$ *Arsenious Acid.*—Take 5 c. c., of $\frac{N}{10}$ arsenious acid, add starch indicator and titrate; (as given under (*a*)).

Reaction.

$$As_2O_3 + 2Na_2O + 4I = As_2O_5 + 4NaI.$$

STARCH INDICATOR.

Take one part of starch, triturate in a mortar with cold water, then pour over it 200 parts of boiling water, and boil a short time; allow it to cool and settle, then draw off the clear liquor for use.

$\frac{N}{10}$ FERROUS SULPHATE.

Weigh out one or two grms. of clean, fine, soft, iron wire, dissolve in dilute H_2SO_4 by the aid of heat, in a small flask closed with a cork through which passes a glass tube drawn out to a fine point at the upper end; when dissolved, transfer to the graduated cylinder, and dilute according to the following proportion:

$$5.6 : 1000 : : \text{wt. taken} : x. \quad x = \text{dilution.}$$

Since pure iron wire cannot readily be obtained, it is necessary to ascertain the per cent. of impurity and deduct the same from the amount taken.

The Ammonio-ferrous Sulphate is a good and convenient substitute for the ferrous sulphate. The formula of this salt is, $Fe(NH_4)_2(SO_4)_2$, $6H_2O$, consequently it contains one-seventh of its weight of iron.

Preparation.—To 50 c. c. of water add 12 c. c. of strong H_2SO_4 and divide into two equal portions. Place one portion in a flask, add a slight excess of small nails, free from rust, and allow the flask to stand in a warm place

over night. In the morning add enough water to restore the solution to its original bulk, warm at 70° C., till the evolution of hydrogen has ceased or nearly ceased, adding water from time to time if necessary; now filter through a warm funnel into a warm dish.

To the other portion add ammonium carbonate in lump till violent action ceases, then warm and add it in powder till the solution is neutral, and filter if necessary. Mix the two solutions in a beaker, heat to 80° or 90° C, mix thoroughly, add a few drops of H_2SO_4 if the solution is not already acid, then pour into a porcelain dish, and stir till cold. Allow to stand some hours, decant the mother-liquor, transfer the bluish-white powder to a funnel and apply suction; wash three or four times with alcohol, and then dry on filter-paper, without heat, till the powder will run like sand. Preserve in ground-stoppered bottles.

$\frac{N}{10}$ AMMONIO-FERROUS SULPHATE.

Take 3.92 grms., add 5 c. c. H_2SO_4, and dissolve in water, and dilute to 100 c. c.

For testing the strength of permanganate or bichromate solutions, take about 0.5 grm. of the iron salt, dissolve in water acidulated with H_2SO_4 and titrate.

$\frac{N}{10}$ SODIUM HYPOSULPHITE.

$Na_2S_2O_3, 5H_2O = 248$. 24.8 grms. per litre.

First powder and dry a quantity of the salt by pressing between folds of blotting paper, then weigh 24.8 grms., dissolve in water, and dilute to one litre.

Directions for titrating are given under "$\frac{N}{10}$ Permanganate and Iodine."

The solution should be kept in the dark; after a time it undergoes a slight amount of oxidation, and sulphur deposits on the bottle. This it is said can be prevented by adding two grms. of Ammonium Sesquicarbonate or a little caustic soda to a litre of the solution.

$\frac{N}{10}$ ARSENIOUS ANHYDRIDE.

$As_2O_3 = 198 \div 4 = 49.5$. 4.95 grms. per litre.

Weigh approximately 3 grms., place it in a flask, add 25 grms. of pure Sodium Bicarbonate, and about 250 c. c. of water; boil till dissolved, cool, decant the clear solution into a graduated cylinder; titrate with $\frac{N}{10}$ Iodine, and calculate the dilution required to make an $\frac{N}{10}$ solution of the As_2O_3. After diluting again titrate with $\frac{N}{10}$ Iodine to make certain of its accuracy.

Box 6.

OXIDE OF IRON.

To be titrated for Fe by $\frac{N}{10}$ $KMnO_4$.
$\frac{N}{10}$ factor of Fe = .0056.

Weigh out 0.5 grm., place it in a porcelain dish, add strong HCl, mix thoroughly, cover with a clock glass and heat at 100° C., till dissolved; cool, then add strong H_2SO_4 and evaporate till SO_3 fumes appear, cool, add water and dilute the solution to a given number of c. c., measure 10 or 20 c. c. into a beaker, dilute with water, add Zn, and enough H_2SO_4 to produce a brisk evolution of hydrogen; warm and allow the action to go on until the Fe_2O_3 is all reduced to FeO, remove the Zn, and heat till the bubbles are all removed, then titrate with $\frac{N}{10}$ $KMnO_4$.

Note: The Zn should always be tested to ascertain if it has reducing power; and if it has, this must be determined, and the amount of $KMnO_4$ which a given weight will reduce, deducted from the total $KMnO_4$ used.

Box 7.

IRON ORE.

To be titrated for Fe by $\frac{N}{10}$ $Na_2S_2O_3$.
$\frac{N}{10}$ factor of Fe = .0056.

Pulverize the sample very fine with an agate mortar, dry at 100° C. then weigh 0.5 grm., digest in a flask with

strong HCl at 100° C. When dissolved, cool, transfer to a graduated cylinder and dilute to 200 c. c.; take 5 c. c., dilute largely, add 3 c. c. of a one per cent. solution of Copper Sulphate, and two drops of KCyS, now titrate with $\frac{N}{10}$ $Na_2S_2O_3$ until the red color disappears.

The solution must be cold, and must remain clear.

The copper is alternately reduced by the Hyposulphite and oxidized by the Fe_2Cl_6.

Also titrate the same solution for Fe in the following manner: Take 5 c. c. boil and run into it from a burette a solution of $SnCl_2$ (50 grms. to 500 c. c. of ½ strength HCl) one drop at a time, till all the Fe_2O_3 is reduced to FeO, and the tin solution is in slight excess; now add 10 c. c. of a cold saturated solution of $HgCl_2$, (60 grms. per litre) shake well, and titrate with $\frac{N}{10}$ $K_2Cr_2O_7$.

Box 8.

FERROUS AND FERRIC OXIDES.

To be titrated for FeO, $\frac{N}{10}$ factor = .0072
To be titrated for Fe_2O_3, $\frac{N}{10}$ factor = .008

Pulverize in an agate mortar, and dry at 100° C.; weigh out 1 grm., place it in the weighing flask, add strong HCl close the flask with a cork, through which passes a glass tube; digest at 100° C till dissolved, cool, and dilute to the mark.

Measure out 10 c. c. and titrate as quickly as possible with $\frac{N}{10}$ $K_2Cr_2O_7$; this will give the FeO.

Measure out 10 c. c.; reduce with $SnCl_2$ and titrate *total* Fe. Deduct the amount of FeO obtained by the first titration and figure the remainder as Fe_2O_3.

Box 9.

ARSENIOUS ANHYDRIDE = 198.

$\frac{N}{10}$ factor of As_2O_3 = .00495
$\frac{N}{10}$ factor of As = .00375

Weigh out 0.2 grm., and dissolve it in 50 c. c. of a saturated solution of pure sodium bicarbonate, with the aid

of heat; cool and dilute to a given number of c. c.; measure out samples, and titrate with $\frac{N}{10}$ iodine and starch.

This method gives the As_2O_3 only and not the As_2O_5 which is always present in the commercial article. If the As_2O_5 is to be estimated it must first be reduced to As_2O_3 by SO_2 gas.

Bottle 10.

TINCTURE OF IODINE.

Iodine = 126.5. $\frac{N}{10}$ factor = .01265.

First test the sample to see whether it is a simple or compound tincture by adding water to a small portion, which will produce a precipitate in the former but not in the latter. If it is a simple tincture, dry the weighing flask, then put into it a few c. c. of the tincture and weigh; now add some KI solution, and dilute to the mark. If it is a compound tincture, weigh without the above precautions, and dilute with water.

Now measure out samples and titrate with $\frac{N}{10}$ $Na_2S_2O_3$, also with $\frac{N}{10}$ As_2O_3.

Bottle 11.

BLEACHING POWDER = $Ca_2H_6O_6Cl_4$.

$\frac{N}{10}$ factor = .003537.

Commercial bleaching powder consists of a mixture of calcium hypochlorite (the true bleaching agent), calcium chloride and hydrate, and in some cases calcium chlorate.

It is generally valued and sold in this country by its per-centage of chlorine.

Weigh 5 grms. and triturate it in a porcelain mortar with water; pour the milky liquid into a graduated cylinder, triturate the residue with water, and repeat the operation till all has been transferred to the cylinder, then dilute to 500 c. c.; shake well and take of the milky liquid 10 c. c., and run into it an excess of $\frac{N}{10}$ As_2O_3 (20 c. c.), shake well, add starch indicator and titrate back the excess of As_2O_3 with $\frac{N}{10}$ Iodine.

BY PRECIPITATION.

$\frac{N}{10}$ SILVER NITRATE.

$AgNO_3 = 169.66$. 16.966 grms. per litre.

Dissolve 4.2418 grms. in water and dilute to 250 c. c.

$\frac{N}{10}$ SODIUM CHLORIDE.

$NaCl = 58.37$. 5.837 grms. per litre.

Dissolve 2.918 grms. in water and dilute to 500 c. c.

$\frac{N}{10}$ AMMONIUM SULPHOCYANATE.

$NH_4SCN = 76$. 7.6 grms. per litre.

This solution cannot be prepared by weighing the salt, owing to its diliquescent nature; therefore dissolve about 4 grms. in 400 c. c. of water and adjust by titrating with $\frac{N}{10}$ $AgNO_3$, (see directions given below).

Indicators.

(*a*) *Normal Potassium Chromate.*—(K_2CrO_4), (it must be free from chlorine). Make a cold saturated solution; it can be used only with neutral solutions and in titrating chlorine in chlorides.

(*b*) *Ammonio Ferric Alum.*—Make a saturated solution.

TITRATION OF SILVER NITRATE.

(1) *With $\frac{N}{10}$ Sodium Chloride.*—Place 5 c. c. of $\frac{N}{10}$ NaCl in a beaker, add 2 drops of indicator (*a*), and titrate with $\frac{N}{10}$ $AgNO_3$ till a faint, permanent red precipitate is formed.

(2) *With $\frac{N}{10}$ Ammonium Sulphocyanate.*—Place 5 c. c. of $\frac{N}{10}$ $AgNO_3$ in a beaker, add 3 drops of indicator (*b*) and about 1 c. c. of HNO_3, titrate with $\frac{N}{10}$ sulphocyanate till a faint permanent red color is produced.

Bottle 12.

SODIUM CHLORIDE.

To be titrated for Cl. $\frac{N}{10}$ factor of Cl = .003537

Dissolve 0.5 grm. in the weighing flask with water, dilute to the mark; measure out several samples and titrate with $\frac{N}{10}$ $AgNO_3$, using indicator (*a*).

Bottle 13.

SILVER NITRATE SOLUTION.

To be titrated for Ag. $\frac{N}{10}$ factor of Ag = .010766

(1) Take 3-5 grms. of solution, and titrate with $\frac{N}{10}$ sulphocyanate, without dilution.

(2) Take known weight of silver solution in a beaker; run in excess of $\frac{N}{10}$ NaCl; add Indicator and titrate back with $\frac{N}{10}$ Ag NO_3.

Bottle 14.

Hydrocyanic Acid, HCN = 27. $\frac{N}{10}$ factor = .0054

Weigh about 5 grms. in a tightly stoppered flask, then add a solution of KHO till decidedly alkaline and dilute largely; now run into the whole solution, $\frac{N}{10}$ $AgNO_3$ till a slight permanent precipitate remains.

Reaction.

$$2KCy + AgNO_3 = KCy,AgCy + KNO_3$$

(no precipitate), $+ AgNo_3$ = precip = $2AgCy + 2KNO_3$

GRAVIMETRIC SEPARATIONS.

Box 1.

SILVER COIN = Ag + Cu (+ traces of Au & Pb).

Clean the sample by washing with KHO, or NH_4OH, then with water, dry, cool, and weigh; place it in the weighing flask, dissolve with HNO_3 (avoiding an excess), cool, and dilute to the mark.

Take 30 c. c. of this solution, heat to 70° C., and add HCl as long as a precipitate is formed (a large excess of HCl must be avoided); stir thoroughly, let it stand in a dark place till the precipitate has fully settled, filter by decantation, wash first with hot water acidulated with HNO_3, then with pure water, dry, etc. (See page 10).

Return the per cent. of Ag.

Boil the filtrate, remove the lamp, add gradually KHO solution till strongly alkaline, boil for 15 minutes, filter and wash by decantation with hot water, until the wash water gives no precipitate with $AgNO_3$. Dry, ignite and weigh. Result = CuO.

Return the per cent. of Cu.

Titrate a portion of the original solution with $\frac{N}{10}$ sulphocyanate, as a check upon the gravimetric determination of the silver.

Box 2.

BRASS = Cu. + Zn. (+ traces of Sn. and Pb.).

Take about 0.2 grm., dissolve in HNO_3, evaporate to dryness, moisten with HNO_3, add water, and heat. If there is a residue, filter.

Res. (*a*) = SnO_2. Dry, ignite and weigh, result = SnO_2; return the per cent. of Sn.

Filt. (*a*) = Cu. Zn. Pb.; add 3 c. c. H_2SO_4, evaporate in a porcelain dish till copious white fumes of SO_3 are given off, cool, add 50 c. c. of cold water; if there is a residue, add 20 c. c. of alcohol, filter and wash with dilute alcohol (1 to 4).

Pp. (*b*) = $PbSO_4$, dry, ignite, cool, add a few drops of H_2SO_4, cover the crucible, heat moderately till excess of H_2SO_4 is driven off; then ignite strongly. Result = $PbSO_4$; return the per cent. of Pb.

Filt. (*b*) = Zn. Cu.; heat on the water bath until the alcohol is expelled, cool, dilute to 100 c. c., add 1 c. c. H_2SO_4, boil then add gradually a solution of sodium hyposulphite (avoiding a large excess) as long as a black precipitate continues to form; filter, and wash thoroughly with hot water.*

Pp. (*c*) = Cu_2S, dry, remove the precipitate from the filter, incinerate the filter thoroughly, add the precipitate, and an equal bulk of sulphur, mix thoroughly, cover the crucible, ignite, moderately at first, finishing with a dull red heat; all the sulphur will be burned off in about 5 minutes.

Result = CuO, Cu_2S; a mixture of the oxide and sulphide. CuO = 79.98 per cent. Cu. and Cu_2S = 79.87 per cent. Cu. Return the per cent. of Cu. treating the result as Cu_2S.

Filt. (*c*) = Zn.; add HNO_3, evaporate to a small bulk, filter to remove the separated sulphur, transfer the filtrate to a large *porcelain* evaporating dish, boil, add a solution of $NaHCO_3$ till strongly alkaline, boil, wash by decantation, and afterwards on the filter with hot water.

Pp. (*d*) = $ZnCO_3$, dry, incinerate the filter, add the precipitate and ignite. Result = ZnO. Return the per cent. of Zn.

Box 3.

PARIS GREEN.

Aceto-arsenite of copper = 3 ($CuOAs_2O_3$), $Cu(C_2H_3O_2)_2$.

* Fresenius 459, Classen 51.

Weigh out 1 grm., add cold NH_4OH, and stir till all the green particles have dissolved. If there is a residue, filter through counterpoised filters.

Res. (*a*) = insoluble matter, dry at 100° C. and weigh. Return the per cent.

Filt. (*a*) = Cu. As; add HCl till nearly neutral, then yellow ammonium sulphide, and digest at a moderate heat for one-half hour, decant the supernatant liquid on a filter, and to the residue add more ammonium sulphide and digest; filter and wash with water, to which a little ammonium sulphide has been added.

Pp. (*b*) = CuS; dry, ignite and weigh.

Result = CuO, Cu_2S. Return the per cent. of Cu.

Filt. (*b*) = As; add dilute HCl, cautiously, to acid reaction; warm, pass H_2S gas for one half hour; filter, (reject the filtrate) dissolve the precipitate with KHO, filter to remove the free sulphur, then pass into the solution chlorine gas, for one hour, (the solution must be kept alkaline), now acidulate with HCl (the solution must remain clear), add NH_4OH in excess, and then magnesia mixture in excess, let it stand 12 hours, filter through tared with filters, wash with a mixture of 1 part NH_4OH and 3 parts water.

Pp. (*c*) = $MgNH_4AsO_4 + 6H_2O$; dry at 102° to 103° C, and weigh; repeat the drying till constant weight is obtained.

Result = $(MgNH_4AsO_4)_2$, H_2O.

Return the per cent. of As.

Box 4.

BAKING POWDER.

The value of a powder depends, *first*, upon the amount of CO_2, which a given weight will give off when dissolved in water; *second*, upon the solution thus formed being neutral; *third*, upon its purity.

Composition of some of the baking powders in common use.

No. 1.		No. 3.	
Corn Starch.....	4 %	Flour.....	37.5 %
Bitartrate of Potash.	58 "	Tartaric Acid	25 "
Bicarbonate of Soda.	38 "	Bicarbonate of Soda	37.5 "
No. 2.		**No. 4.**	
Corn Starch.....	37 %	Flour.....	20 %
Tartaric Acid.....	10 "	Bitartrate of Potash.	51 "
Bicarbonate of Soda.	30 "	Tartaric Acid.....	3 "
Sesqui Carb. Am....	6 "	Bicarbonate of Soda.	24 "
Alum.....	17 "	Carbonate of Am....	2 "

These are known as tartaric acid or cream of tartar powders; the alum in No. 3 is probably used to make the bread white and performs no other part in the powder.

There are, besides the foregoing powders, those which have no tartaric acid.

First, the alum powders, which should always be rejected.

Second, the phosphate powders, which are said to be among the best.

The following directions apply only to the tartaric acid or cream of tartar powder, which should always be tested for adulterations, especially alum; and if present it should be estimated.

(1) *Estimation of Starch or Flour*—Take 0.5 grm., add cold water and shake till the powder is dissolved, filter through tared filters, dry at 100° C, and weigh.

The filtrate after boiling should give a neutral reaction when tested with litmus.

If it gives an alkaline reaction, which is often the case, titrate this excess of alkali with $\frac{N}{10}$ H_2SO_4, and calculate the excess as $NaHCO_3$.

(2) *Estimation of* CO_2.—(*a*) Use the ordinary carbonic acid apparatus, and displace the CO_2 with dilute H_2SO_4; this gives the total CO_2.

(*b*) Determine the CO_2 which the powder will give off when dissolved in water using the same apparatus; heat the flask to 80° C at the last, and cool before weighing; this gives the available CO_2.

(3) *Estimation of Soda and Potash.*—First test for potash with the flame. Take 1 grm. incinerate thoroughly in a porcelain evaporating dish till the carbon is all burnt off, (the mass must not be fused). Extract the residue with hot water, filter into a flask (the filtrate should not exceed 30 c. c.) If there is no potash present titrate this filtrate with $\frac{N}{10}$ H_2SO_4 for soda. If potash is present, place the flask containing this filtrate over the lamp, boil, and while boiling add gradually from a burette normal tartaric acid, until the red color of the indicator fails to reappear after boiling two minutes, now add as much more tartaric acid, cool the solution, etc. (See page 21).

(4) *Estimation of Tartaric Acid.*—Since this cannot be estimated advantageously by any direct process, we resort to an indirect method by calculation.

If the tartaric acid exists in the powder in the form of bitartrate of potash, the following proportion will give the amount of that salt present.

KHO : $C_4H_5KO_6$: : the per cent of KHO : x. x = the per cent. of bitartrate of potash.

If there is no potash present then we may conclude that the tartaric acid exists as such in the powder, and its per cent. may be thus calculated. Deduct from the total NaHO as found by (3), the excess, if any, of NaHO as found by (1); the difference represents the amount of NaHO, neutralized by the tartaric acid. Placing it in the form of a proportion, we have.

2(NaHO) : $C_4H_6O_6$: : the per cent. of NaHO : y. y = per cent. of tartaric acid.

Return the ingredients as found by the foregoing directions as follows:

Starch or Flour.....	per cent.
Total Bicarbonate of Soda ($NaHCO_3$).....	" "
Excess of " " " "	" "
Bitartrate of Potash ($C_4H_5KO_6$) or.....	" "
Tartaric Acid ($C_4H_6O_6$).....	" "

Also report what if any impurities are present.

WATER ANALYSIS.

REAGENTS AND APPARATUS.

[*A*] *Reagents for the estimation of nitrogen, present as ammonia* (NH_3).

(1) *Nessler Reagent.*—Take 5 grms. KI, dissolve in 15 c. c. of water, add gradually, a cold saturated solution of mercuric chloride (table reagent), till the mercuric iodide ceases to be dissolved on stirring, and a slight permanent precipitate remains; now add a solution of caustic potash, made by dissolving 15 grms. of solid caustic in 30 c. c. of water; allow to settle before using.

(2) *Dilute Solution of Ammonia.*—Dissolve 3.15 grms. of NH_4Cl in one litre of water. Take 10 c. c. of this solution and dilute to one litre. .1 c. c. of this solution contains .00001 grm. of NH_3.

(3) *Dry Sodium Carbonate.*—Heat about 3 grms. of anhydrous sodium carbonate in a porcelain dish for one hour, at a bright red heat, cool, pulverize and place in a ground stoppered bottle.

(4) *Apparatus.*—Four large test tubes, of the same diameter, that will hold 60 c. c. or more. Graduate with a 50 c. c. mark. Also a glass tube with a bulb blown at one end.

[*B*] *Reagent for the estimation of Albumenoid Ammonia.*

(1) *Solution of Potassium Permanganate and Potash* —is made by dissolving 1. grm. of $KMnO_4$, and 25 grms. of solid caustic potash in separate portions of water, mixing the solutions and diluting to 125 c. c.; boil the solution for one-half hour, cool and place in a well stoppered bottle.

[*C*] *Reagents for determining hardness.*

(1) *Solution of Calcium Chloride.*—Dissolve 1 grm. of finely powdered marble, or pure carbonate of lime in a slight excess of dilute HCl, and neutralize the excess of acid by ammonia, and dilute to one litre. Each c. c. contains .001 grm. $CaCO_3$.

(2) *Soap Solution.*—Dissolve about 8 grms. of white castile-soap (or any good olive-oil soap) in 600 c. c. of 35 per cent. alcohol, and so dilute it that 13 c. c. will produce a permanent lather in 70 c. c. of distilled water which contains 12 c. c. of C. 1. It has been found that 70 c. c. of pure water destroy 1 c. c. of standard soap; and since we use 70 c. c. of the water under examination it will destroy 1 c. c. of soap, without any material being present which causes hardness. To compare the solutions proceed as follows:

Take 12 c. c. of C. 1, place it in a 200 c. c., flask and add 58 c. c. of pure water ($12 + 58 = 70$); now run in from a burette the soap solution, 1 c. c. at a time, and shake the flask after each addition, till a lather is produced which will last five minutes. From the result obtained calculate the dilution required. Suppose 8 c. c. of the soap solution were used and there are 600 c. c. remaining in the graduated cylinder. We must dilute the 600 c. c. so that, 13 c. c. will be required instead of 8 c. c. The following proportion will give the amount of 35 per cent. alcohol that must be added.

$8 : 5 : : 600 : x = 375$ c. c. to be added or $600 + 375 =$ 975 c. c. total dilution.

[*D*] *Reagents for determining Cl, present as chlorides.*

(1) *Silver Nitrate.*—Dissolve 4.79 grms. of $AgNO_3$ in one litre of pure water; one c. c. will precipitate .001 grm. Cl.

(2) *Yellow Potassium Chromate.*—Make a cold saturated solution (it must be free from chlorine).

COLLECTION OF SAMPLES.

The amount to be collected will depend upon the nature of the water and the number of elements to be

determined; two gallons as a rule will be ample. Care must be exercised in collecting the sample to secure an average. The bottle, in which the sample is to be collected, should be first thoroughly cleansed, and then rinsed out with some of the same kind of water as that which is to be analyzed; after filling, it should be closed with a clean cork.

Before taking out a sample for any of the following determinations, the bottle should be well shaken, unless otherwise directed.

Determination of the Total Solid Residue.

Take 100 c. c. and evaporate to dryness in a weighed dish, on a water-bath, then place in an air-bath and heat at 104° C for 30 minutes, cool and weigh. Result = total solid residue.

A much larger quantity of water will be required in most cases.

For the sake of convenience, convert all results as fast as obtained into parts per 1,000.

Determination of Chlorine.

Take 100 c. c., add a few drops of D. 2, and titrate with D. 1.

If good results are not obtained, take 500 c. c., concentrate by evaporation to about 50 c. c. and then titrate.

Both solutions must be neutral; if acid, make neutral by adding some carbonate of soda.

Determination of Sulphuric Acid.

Take 200 c. c., acidify with HCl, boil, filter, and then precipitate with barium chloride.

Determination of Inorganic Constituents.

Acidulate one litre with HCl, and evaporate to dryness, moisten the residue with HCl and dissolve with water, filter.

Res. (*a*) = SiO_2; dry, ignite and weigh.

Filt. (*a*); concentrate by evaporation, add excess of ammonia, boil, filter.

Pp. (*b*) = Fe_2O_3—Al_2O_3 and P_2O_5. Dry, ignite and weigh.

Filt. (*b*); add excess of ammonium oxalate, boil, let stand six hours, filter.

Pp. (*c*) = calcium oxalate, dry, ignite and weigh.

Filt. (*c*); concentrate, cool, add a solution of Na_2HPO_4 and NH_4OH in excess, let stand six hours, filter.

Pp. (*d*) = $Mg_2(NH_4)_2(PO_4)_2$. Dry, ignite and weigh.

Determination of Potash and Soda.

These are generally determined jointly.

Take 500 c. c. evaporate to dryness, add 0.2 grm. of caustic baryta, and a little distilled water, and boil, filter; to the filtrate add ammonium carbonate, boil and filter; evaporate this filtrate to dryness and ignite moderately in a weighed porcelain crucible; remove the lamp, add solid NH_4Cl, and again ignite till fumes cease to be given off (use only a moderate heat) cool and weigh.

Result = KCl, NaCl, return as Na_2O.

Determination of Hardness.

Take 70 c. c. of the sample of water, place it in a 200 c. c. flask, then run in from a burette soap solution, 1 c. c. at a time, shaking the flask after each addition, till a lather is produced which will last five minutes, and will reappear on shaking. The number of c. c. of soap solution used represents the degrees of hardness; and each degree stands for one grain of $CaCO_3$, or its equivalent, in an English gallon.

The English gallon hold 70,000 grains.

The United States gallon holds 58,318 grains.

If the 70 c. c. require more than 16 c. c. of the soap solution, then take 35 c. c. of the water, and add to it 35 c. c. of distilled water, and titrate with the soap solution; the result multiplied by two will give the degrees of hardness.

Further dilution may be required to reduce the amount of soap solution required below 16 c. c.

The reason why this dilution is called for, appears to be that too large a proportion of insoluble lime-salts, interferes with the formation of a lather. When the water contains much Magnesium, which is known by the lather having a curdy appearance, the reaction is slow, and the water should be diluted so much, that 70 c. c. will require less than 7 c. c. of the soap solution. Time should be given for the Magnesium salt to form.

Determination of Ammonia.

Place a well washed litre flask upon a piece of wire gauze, which rests upon the ring of the lamp-stand, and then connect it with a Liebig's condenser. Pour into this flask 500 c. c. of the sample of water, and add to it one grm. of the ignited sodium carbonate, connect the apparatus, and distil rapidly, collecting the distillate in the graduated test tubes (A-4). Distil until four tubes have been filled to the 50 c. c. mark, then stop the operation. Now Nesslerise the second tube, thus: add to it 2 c. c. of Nessler reagent and thoroughly mix; if ammonia is present, it will assume a rich brown color; and the more the ammonia, the deeper the color. Take another test tube, (A-4) place in it 1 c. c. of the dilute NH_4Cl (A-2), and make up to 50 c. c. with distilled water, mix thoroughly, add 2 c. c. Nessler reagent and again mix; compare this with the Nesslerised distillate. If the colors are not the same, the made up tube must be emptied, rinsed, and refilled, in the same order, adding more or less of the dilute NH_4Cl, as it was lighter or darker than the distillate. This operation must be repeated till the colors are the same. The amount of dilute NH_4Cl, added to the made up tube represents the amount of NH_3 in the distillate, the Nesslerising of this second tube, is to find out whether the first tube can be Nesslerised as a whole, or must be divided. If 1 c. c. of the dilute NH_4Cl has been used, then the first tube cannot be Nesslerised as a whole, for it would give too dark a color.

Therefore take 10 or 20 c. c. of the first tube, make it up to 50 c. c. with distilled water, mix thoroughly, add 2 c. c. Nessler Reagent and again mix; compare with a made up tube as before; the result multiplied by the proper factor will give the total NH_3 in the first tube; add to this one-third, and we obtain the total free ammonia.

Thus, 10 c. c. of the first tube gave .00001 grm. NH_3, multiplied by 5 gives .00005 grm. in the first tube; add to this one-third and we have .000067 grm. NH_3 in the 500 c.c. taken, or .000134 grm. in a litre.

*ESTIMATION OF TOTAL NITROGEN OF NITRATES AND NITRITES.

Reagents; (To be prepared shortly before required for use).

(1) Nessler's Reagent.

(2) Solution of NH_4Cl.

(3) Saturated Solution $H_2C_2O_4$, nearly free from NH_3. It should be tested for NH_3 before using. A *slight* color when Nesslerized may be disregarded.

(4) Zn–Cu couple. Fill a wide mouthed quart bottle with solution of $CuSO_4$ in H_2O, containing 1.4 to 1.8 per cent $CuSO_4$. Clean several strips of sheet Zinc, four inches by three-fourths of an inch in size, in dilute H_2SO_4 and rinse carefully with pure H_2O. Introduce same into the solution of $CuSO_4$ and close the bottle—set aside till the Zn is well coated with Cu. Carefully remove the strips of metal with forceps and wash with successive portions of pure H_2O, being careful not to break off the coating of Cu.

Method.

200 c. c. of the H_2O under examination are barely acidulated with Reagent, 3 (above) and thoroughly mixed. Divide into two equal portions and place each 100 c. c. in

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*This method, called the Williams-Blunt method, has been discussed at length, by Dr. A. B. Prescott, in the Pharmaceutical Era for 1887, and the method, as herein given, is taken from that source.

a wide-mouthed bottle. Into one portion insert one of the prepared Zn–Cu plates. Close both bottles and set aside in an atmosphere free from NH_3 for from 24 to 40 hours.

Great care should be taken to rinse all apparatus used in pure, Ammonia—free H_2O. Take from 10 to 50 c.c. from each bottle (if the H_2O has not over ½ part per million of Nitrogen of Nitrates and Nitrites, 50 c. c.'s may be taken, but if there be 1 part per million, or over, *less* of the H_2O, say 10–20 c. c. may be taken and diluted, with pure H_2O, up to 50 c. c.) care being taken not to disturb any sediment of precipated oxalates which may be in the bottom. If less than 50 c. c. be taken from *each* bottle, the *same quantity* must be taken from each, and diluted to 50 c. c. with the *same* ammonia—free H_2O.

Treat both portions of H_2O with Nessler's Reagent (enough to serve the purpose after the $H_2C_2O_4$ has been neutralized) and titrate the sample, in which Nitrates and Nitrites have been reduced, against the other sample. The excess found in the reduced portion will be the Nitrogen of Nitrates and Nitrites. No account being taken of the Ammoniacal Nitrogen, discovered by Nesslerizing the unreduced portion, which is estimated in another operation.

Nitrites remain to be tested for—which may be done by use of Napthylamine Hydrochloride and Sulphanilic acid. If Nitrites are discovered their Nitrogen is to be estimated and deducted from the amount found by the last operation. The color titration of Nitrites with Napthylamine hydrochloride is a valuable method, and but little practice in comparison of *known* solutions is necessary to render the operator comparatively expert.

The results of the above determinations should be calculated and reported as (1) Nitrogen of *Nitrates*, and (2) Nitrogen of *Nitrites*.

DETERMINATION OF ALBUMENOID AMMONIA.

From the 500 c. c. of water taken we have distilled off

200 c. c. for the estimation of *free* Ammonia; in the remaining 300 c. c. we estimate the "organic" or *albumenoid* Ammonia, as follows:

Take 50 c. c. of Permanganate solution (B-1) and add to it 200 c. c. of pure ammonia-free water; distill till the distillate gives no color with Nessler's Reagent. Then add to this solution, in the retort, the 300 c. c. of the water under examination and distill for albumenoid Ammonia. Collect the whole distillate, of 150–200 c. c., mix thoroughly, measure and take portions of 10–100 c. c. (according to the amount of NH_3) and Nesslerize.

By the above dilution of the $KMnO_4$ solution it gives up, upon distillation, the small amount of Ammonia which it otherwise would retain and which would of course vitiate the result.

Reports.

Results obtained are generally reported as "parts per million" and also as "grains per gallon." The United States gallon contains, at 60° F., 58,318 grains of distilled water. To convert "grammes per Litre" into "grains per gallon," multiply by 58,318 and divide by 1,000.

Report "*free* Ammonia" and "*albumenoid* Ammonia"; also, "Nitrogen of Nitrates" and "Nitrogen of Nitrites."

METHODS OF ESTIMATING THE ORGANIC IMPURITIES IN WATER WITHOUT GAS APPARATUS.

THE OXYGEN PROCESS.

Reagents.

(a) *Standard Solution of Potassium Permanganate.*—Dissolve 0.395 grms. of potassium permanganate in 1 litre of water. Each c. c. contains 0.0001 grm. of available oxygen.

(b) *Standard Solution of Sodium Hyposulphite.*—

Dissolve 3.068 grms. of the salt in 1 litre of water. 1 c. c. = 1 c. c. of the permanganate solution.

(c) *Solution of Potassium Iodide.*—One part of the pure salt, recrystallized from alcohol, dissolved in ten parts of water.

(d) *Dilute Sulphuric Acid.*—One part by volume of pure sulphuric acid is mixed with three parts by volume of water, and solution of potassium permanganate added until the whole retains a very faint pink tint, after warming to 80° F for four hours.

(e) Starch Indicator, (see page 20).

Determination of the Oxygen Absorbed by the Water.

Select a half litre glass-stoppered flask and clean thoroughly with H_2SO_4 and water. Put 250 c. c. of the water into it, stopper tightly and immerse in a water or air bath until the temperature rises to 27° C. Now add to it 10 c. c. of the sulphuric acid (Sol. d), and then 10 c. c. of the standard permanganate (Sol. a). Stopper tightly and allow it to remain at 27° C, for 4 hours, remove and add the solution of potassium iodide till the pink color disappears, then shake thoroughly and titrate with hyposulphite solution until the yellow color is nearly distroyed, then add a few drops of starch indicator, and continue the titration till the blue color is just discharged. The c. c. of $KMnO_4$ taken, less the c. c. of hyposulphite used = the c. c. of $KMnO_4$ reduced. Should the permanganate color fade rapidly during the four hours, other measured quantities must be added from time to time.

The permanganate and hyposulphite solutions must be compared often, and a correction factor used if necessary in the titration.

CONCLUSIONS.

The purity of the water is indicated by the amount of Oxygen absorbed from the permanganate by 100,000. parts of H_2O. The following figures (which must be considered

as of *questionable value*) have been given in connection with the foregoing process:

"Water of great organic purity absorbs 0.05 parts of Oxygen."

"Water of medium purity absorbs 0.05 to 0.15 parts of Oxygen."

"Water of doubtful purity absorbs 0.15 to 0.2 parts of Oxygen."

"Impure water absorbs 0.2 or more."

Regarding the foregoing process as a means of *definite decision* as to the sanitary character of a water, it is now generally conceded that *alone* it is of *no value*, but should always be considered as simply an auxiliary estimation, to be considered together with the estimation of saline constituents, free and albumenoid ammonia, Nitrates and Nitrites, etc., etc.

In concluding this section concerning Water Analysis it is necessary to state that the interpretation of the results of an analysis of water is a matter of far too extensive a character for the scope of this book, and it will not be attempted, but, with a few of the elementary considerations necessary in forming an idea of the character of a water, the subject will be left to the student, as one which requires a vast amount of study and research.

In the examination of a water, its *source* should be known—whether from a cistern, well or hydrant; also, the proximity of any possible source of contamination, the geological character of the country and the character of the soil and sub-soil. Un-polluted spring water usually contains less than *one* part of Chlorine. Sewage generally contains from 10 to 14 parts of Chlorine.

The amount of Albumenoid Ammonia is of great importance, since it indicates the presence of undecomposed animal or vegetable matter.

The *free* NH_3, the Nitrates and Nitrites may be considered harmless *in themselves;* yet, as being products of

the oxidation of organic matter, they indicate the *possibility* of evil, should the certain conditions of temperature, filtration, etc. (which oxidize the organic matter) be removed or fail to exert their influence.

A microscopic examination, both of the water and residue on evaporation, is often employed with profit, and, in some cases, valuable data may be determined from the *appearance* of the residue after evaporation and its *odor* upon ignition.

SELECT METHODS

IN

QUANTITATIVE ANALYSIS.

PART II.

USE OF PLATINUM VESSELS.

The following bodies should not be treated in platinum vessels.

1. The caustic alkalies as well as baryta and strontia.

2. Fusible metallic sulphides, or mixtures of sulphides with carbon; especially the alkaline sulphides.

3. Phosphates and carbon, which at a high heat form platinum phosphide.

4. Metals that are easily fused, or metallic oxides that are easily reduced. These form fusible alloys with platinum.

5. Chlorine, and all mixtures that liberate chlorine, either in the cold or by heat; as fusible mixtures of a metallic chloride and a nitrate, of ammonium sulphate and a chloride.

Platinum crucibles may be cleaned by fusing borax or potassium bisulphate in them, and dissolving the fused mass with boiling water. Sometimes they may be cleaned by digesting with dilute HCl. To brighten them scour with sea-sand and water; do not use sharp sand or emery.

SELECT METHODS IN QUANTITATIVE ANALYSIS.

LIMESTONE.

For technical purposes, it is sufficient to determine those constituents which perform the active part in any given operation.

The more common constituents of limestone may be determined as follows:

Pulverize a few grms., dry at 100° C. Weigh 1 grm. of the dry sample, transfer it to a porcelain dish, cover with a clock-glass, add 20 c. c. of water, then 10 c. c. of HCl, and 2 c. c. of HNO_3, heat till effervescence ceases, then boil and filter. (For complete separation of the silica evaporate to dryness on the water bath. When perfectly dry, cool, moisten with HCl, add water and heat until dissolved, then filter.*)

Res. (*a*) = Silica and silicates; dry, ignite and weigh; and return as insoluble matter. If it is desired to estimate the elements of this insoluble matter, mix the ignited residue with Ammonium Fluoride, cover the crucible and ignite till fumes cease to be given off, repeat this operation till constant weight is obtained. The difference between the first and last weight is the silica. Transfer the residue from the crucible to a beaker and dissolve in strong HCl, and add the solution to filtrate (a).

Filt. (*a*); add 10 c. c. HCl, then ammonia to slight alkaline reaction, and boil till excess of ammonia is expelled, filter.

Pp. (*b*) = iron, alumina, and phosphoric acid. If this precipitate is small, it may either be rejected or returned

*Classen 32.

as a whole; if large, separate, and estimate the per cent. of iron and alumina.

Filt. (*b*), add ammonium oxalate in excess, (there must be sufficient to form an oxalate of all the magnesia present), heat just to boiling, and then allow it to stand in a warm place for six hours; filter by decantation, wash once with water in the same way; now dissolve the precipitate in dilute HCl; add a little ammonium oxalate, and then ammonia in excess; boil, filter and wash by decantation. The re-precipitation is to separate the magnesia which is precipitated with the lime in the first operation.

Pp. (*c*) = calcium oxalate.

Filt. (*c*), (The united filtrates); concentrate by evaporation, (adding HCl if necessary, to prevent the formation of a precipitate), cool, add ammonia in excess, then sodium ammonium phosphate, and allow to stand six hours in a cool place; filter and wash with water containing ammonia.

Pp. (*d*) = $Mg_2(NH_4)_2(PO_4)_2$.

ESTIMATION OF CO_2.*

Fuse 2 grms. of vitrified borax in a platinum crucible, cool in a desiccator, and weigh; add about 0.5 grm. of the well dried limestone and weigh; then apply heat and gradually increase to redness and continue the heat till the mass is in a state of quiet fusion, cool and weigh. The loss in weight is the CO_2.

Volumetric Estimation of Calcium.†

Weigh 1 grm. and dissolve in dilute aqua regia, cool add a slight excess of ammonia, then a large excess of ammonium oxalate; heat just to boiling and then allow it to stand till the precipitate has subsided; filter and wash thoroughly by decantation, till the ammonium oxalate

* Fresenius 336.

† Sutton 133.

has been removed. Place beneath the funnel a 250 c. c. flask, pierce the filter, wash the precipitate into the flask, first with water, then with dilute sulphuric acid or HCl; then add to the contents of the flask enough dilute sulphuric acid to dissolve (or decompose) the calcium oxalate, and dilute to 250 c. c. Titrate portions of this solution with $\frac{N}{10}$ $KMnO_4$.

The $\frac{N}{10}$ factor of CaO = .0028.

Note.—If there is much magnesia present, the calcium oxalate should be dissolved in dilute HCl and re-precipitated.

IRON ORE.

Estimation of Iron, Silica and Sulphur.

Weigh from 2 to 5 grms. of the dry ore, mix it thoroughly in a clock-glass with five times its weight of the fusing mixture. Select a large platinum crucible, and fuse in it 2 grms. of the fusing mixture, when well fused lower the crucible into the flame of the Bunsen burner so that the bottom becomes cool and the heat is upon the sides; remove the lamp, introduce into the crucible one-third of the ore mixture, cover the crucible and replace the burner, and continue the heat till the mass has become quiet; now introduce another third and treat it in the same way; and finally the last third; continue the heat till the mass has become quiet, then apply the heat to the bottom of the crucible, and finally apply the heat of the blast-lamp until reduced to quiet fusion.* Sometimes a semi-fused mass results which cannot be made fluid by the strongest heat. Remove the lamp and incline the crucible as much as possible, and rotate it as the mass solidifies; while still hot plunge it sidewise into a beaker of cold water, remove it, and, after a few seconds plunge

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*Fresenius 383.

again; repeat this three or four times. Then place the crucible on its side in the beaker, and heat till the mass separates, remove the crucible, and continue the heat till the mass is disintegrated; filter and wash with hot water by decantation.

Res. (*a*) contains the iron, alumina, etc. Dissolve in HCl, upon a water bath; if it fails to dissolve, filter and re-fuse the insoluble portion; when all is dissolved except the silica, evaporate to dryness, moisten with HCl and take up with water; filter.

Res. (*b*) = part of the silica.

Filt. (*b*), dilute to a given number of c. c. and estimate in one portion the iron and alumina together, and in another the iron by titration.

Note.—An alcohol lamp should be used if possible for the fusion. If gas is used, it should be passed through a solution of potash to remove the sulphur before burning.

Filt. (*a*). Add HCl cautiously till acid, evaporate to dryness, heat on an iron plate to 110° C; moisten the residue with HCl, add water and boil; filter.

Res. (*c*) = silica. Dry and ignite residues (c) and (b) together.

Filt. (*c*). Boil, and add a boiling solution of barium chloride; filter after standing over night, and determine the sulphur in the precipitate.

Titration—of the iron in filt. (b).

Take a portion of the filtrate, add HCl till strongly acid, boil, and run into it from a burette stannous chloride, very cautiously, till the Fe_2O_3 is reduced to FeO. and the $SnCl_2$ is in slight excess. (When the reduction is complete the solution will be colorless); now add 5 c. c. of a saturated solutiod of $HgCl_2$, and titrate the iron with $\frac{N}{10}$ $K_2Cr_2O_7$.

For the estimation of manganese, lime, and magnesia, dissolve about 1 grm. of the ore, according to the directions given below for the estimation of phosphorus, separate the iron and alumina from the other bases as basic

acetates,* and the manganese with bromine or ammonium sulphide.†

Estimation of Phosphorus.

Weigh 5 grms. of the fine dry ore and digest at 100° C., with strong HCl, till all, or nearly all is dissolved; then boil for 15 minutes, filter and wash slightly.

Res. (*a*). Place the filter with its residue in a platinum crucible, incinerate thoroughly; cool, add dry Na_2CO_3 and fuse; dissolve in dilute HCl, and add this solution with its residual silica to filtrate (a).

Filt. (*a*). Evaporate to dryness, and heat on an iron plate at 110° C., till it no longer emits an odor of HCl; cool slightly, add strong HCl and boil till the iron is dissolved; evaporate as low as possible without formation of oxide of iron, then add 30 c. c. of HNO_3 (1.42 sp. gr.) and evaporate to a sirupy consistence, then add more HNO_3 and repeat till HCl is driven off; now add an equal volume of water, cool and filter.

Filt. (*b*). Precipitate the phosphoric acid according to directions given on page (60).

Res. (*a*) and *Filt.* (*a*) may be worked separately and if no phosphorus is found in res. (a) it may be neglected in the analysis of ore from that mine. If phosphorus is found in res. (a), the amount may be determined in several samples of ore, and then neglected in other samples from that mine; the amount thus found being added to that obtained from filt. (a), in all subsequent determinations.

Estimation of Iron.

Place 0.5 grms.‡ of the *very fine* dry ore in a 4 oz. Erlenmeyer flask, add 15 c. c. of strong HCl, mix thor-

* Fresenius 429.

† Fresenius 430—203. Classen 73.

‡ Or, better, weigh exactly 0.560 grms. ore, dissolve in 15-20 c. c. strong HCl, (in a small beaker which has no lip and which should be closely covered with a watch-glass) letting substance digest for some

oughly, place the flask on an iron plate and heat at from 80° to 90° C., till dissolved; now add 10 c. c. of water and run in stannous chloride solution, one drop at a time, shaking after each addition, till the iron solution is colorless, now transfer to a large flask and dilute to about 400 c. c. with water, then add 10 c. c. of a saturated solution of $HgCl_2$, which should produce a silky white precipitate. Titrate this solution with $\frac{N}{10}$ $K_2Cr_2O_7$. Or add to this solution 10 c. c. of a cold saturated solution of manganous sulphate and titrate with $\frac{N}{10}$ $KMnO_4$; the end reaction is reached when the pink color first permeates the whole solution. In titrating with $\frac{N}{10}$ $KMnO_4$ it is better to use only 0.2 grms. of ore.

Estimation of Sulphur.

*First Method.** Place 1 grm. of the fine dry ore in a porcelain dish, add 0.5 grms. of pulverized $KClO_3$, pour over it 50 c. c. HNO_3 (1.42 sp. gr.) and cover with a funnel or clock-glass; now place it over the lamp and raise the heat gradually and bring to a boil and boil for fifteen minutes, adding from time to time crystals of $KClO_3$; now remove the cover and evaporate to a small bulk, then add strong HCl and evaporate to dryness on a water bath. Moisten the residue with strong HCl, add water, boil, then filter and wash thoroughly; nearly neutralize the filtrate with ammonia, boil, add 5 c. c. of *the* tartaric acid solution, and sufficient $BaCl_2$ solution to precipitate the sulphur, boil, then allow it to stand all night, filter, wash thoroughly with hot water, then with a dilute solution of ammonium acetate to dissolve any barium nitrate which may adhere to the sulphate.

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time at a slight heat and finishing by boiling. To the hot, concentrated solution add solution of $SnCl_2$ to *exact* decolorization, wash into a 400 c. c. beaker, add 15–30 c. c. of solution of $HgCl_2$, dilute *largely* with H_2O and titrate with $\frac{N}{10}$ $K_2Cr_2O_7$. Each c. c. of $K_2Cr_2O_7$ — 1 per cent. (F. C. S.)

*Crooks 480.

Second Method. Place 1 grm. of the fine dry ore in a 4 oz. Erlenmeyer flask, moisten thoroughly with the smallest quantity of water possible, then add about 3 c. c. of bromine and shake thoroughly; now heat at 80° C., for 5 minutes, then add 15 c. c. of strong HCl and continue the heat 15 minutes longer, transfer to a porcelain dish and evaporate to dryness on a water bath, etc. (see page 52).

Estimation of Manganese.

Take 5 grms. of the ore, dissolve in strong HCl, cool, add H_2SO_4 in slight excess, evaporate till HCl is all expelled, cool, add water, heat till dissolved, transfer to a 500 c. c. flask; dilute largely, add zinc oxide in excess, dilute to the mark, shake thoroughly, filter off a portion through a ribbed filter; boil a measured portion of this filtrate, and titrate with $\frac{N}{10}$ $KMnO_4$, (see page 70).

COAL.

Proximate Analysis of Coal.

Pulverize a sample of the coal in a rough, porcelain mortar.

Determination of Moisture.—Take 1 grm. place it in a covered crucible, and heat in an air bath at 115° C. for one hour, cool and weigh. Loss = Moisture.

Determination of Volatile Matter.—Take 1 grm. of the undried coal, place it in a platinum crucible, and cover tightly; heat it for three and a half minutes over a Bunsen burner, and then without cooling, for the same length of time, over a blast lamp, cool and weigh. Loss, less the moisture = volatile matter and one-half of the sulphur present as sulphide of iron.

Determination of Fixed Carbon.—Incinerate the residue from the last operation until the carbon is burnt off

and a constant weight is obtained. Loss = fixed carbon and one-half of the sulphur present as sulphide of iron. The last weight is the ash.

Estimation of the Total Sulphur.

Reagent. Mix thoroughly 4 grms. of calcined magnesia and 2 grms. of anhydrous sodium carbonate, and determine the sulphur in the mixture. Weigh 1 grm. of the very fine coal and mix it thoroughly with 2 grms. of the reagent in a porcelain crucible, which should not be more than two-thirds full. Place the crucible in an inclined position on a triangle, and heat very gradually, with an alcohol lamp, increasing the heat until the bottom is dull red. (The heat must not, in any stage of the operation, be so high as to fuse the mass). Stir the mixture with a platinum wire to hasten the combustion, which requires about one hour. When the carbon is all oxidised, remove the lamp and allow the crucible to stand until perfectly cold, then add 1 gram of pulverized ammonium nitrate, mix thoroughly and heat for 5 or 10 minutes at a red heat. Cool, dissolve in water and dilute to about 150 c.c.; acidulate with HCl, warm, and filter. Boil the filtrate and add a hot solution of $BaCl_2$; allow it to stand one hour, then filter, etc.

Estimation of Sulphur,—present as calcium sulphate.

Take 4 grms. of the coal, add 6 grms. sodium carbonate (which must be free from sulphur), then add water and boil for two hours, replacing the evaporated water. Filter, acidulate the filtrate and precipitate the sulphuric acid in the usual way.

Phosphoric Acid.

If present in the coal, it will be found in the ash, and should be estimated in the usual manner.

BLAST FURNACE SLAG.

The slag may contain,—FeO, Fe_2O_3, FeS, MnO, Al_2O_3, CuO, PbO, ZnO, CaO, MgO, K_2O, Na_2O, SiO_2, TiO_2, SO_3, P_2O_5, CaS.

Scheme for Analysis.

The slag when not soluble in HCl, is decomposed by fusion. (See directions for fusing iron ore for the estimation of iron, silica, and sulphur, page 47).

Res. (*a*) = silica and titanic acid. (It will contain most of the TiO_2, if too large an amount of HCl has not been used in taking up the residue.)

Filt. (*a*) = all the bases acids (also some SiO_2 and TiO_2). Reduce the ferric to ferrous iron by sulphurous acid and then pass through the solution H_2S gas, and filter.

Pp. (*b*) = PbS, CuS, As_2S_3. (If there is any arsenic in the slag, it will, as a rule, be volatilized in preparing the solution and will not appear at this point). The copper and lead can best be separated by sulphuric acid and alcohol.

Filt. (*b*). Add HCl, boil, then add a few crystals of $KClO_3$ and continue the boiling until the odor of Cl has disappeared; now dilute the solution to 600 or 800 c. c. and precipitate the iron and alumina as basic acetates and filter.

Pp. (*c*) = Fe_2O_3, Al_2O_3, SiO_2 TiO_2, P_2O_5. Pierce the filter and wash the precipitate into a beaker, and dissolve in sulphuric acid; nearly neutralize with NH_4OH, dilute if necessary, pass H_2S gas till the Fe_2O_3 is reduced to FeO, boil for some time, replacing the evaporated water; filter.

Pp. (*d*) = SiO_2, TiO_2. Add this prcipitate to residue (a).

Filt. (*d*). Add HNO_3, and boil till the iron is oxidized, filter if necessary, dilute to a given number of c. c. and estimate the iron and alumina in one portion, and the iron in another portion by titration.

Filt. (*c*). Concentrate to 200 c. c. Add acetic acid and pass H_2S gas; filter.

Pp. (*e*) = ZnS. Dissolve in HCl; filter out the sulphur, and precipitate the zinc with sodium bi-carbonate in a porcelain dish.

Filt. (*e*). Concentrate to 200 c. c. by boiling, filter if necessary and precipitate the manganese with bromine,

Pp. (*f*) = manganese.

Filt. (*f*). Add ammonia till alkaline, boil and add ammonium oxalate, filter.

Pp. (*g*) = CaC_2O_4.

Filt. (*g*) = MgO, precipitate with sodium ammonium phosphate.

Res. (*a*) + *Pp.* (*d*); dry, ignite and weigh; treat the ignited residue with ammonium fluoride, and weigh the residual TiO_2; or separate the SiO_2 and TiO_2 by fusing with fused $KHSO_4$.

Estimation of Phosphoric Acid and Sulphur.—See directions for estimating these in iron ore.

Estimation of Silica.

Slags which have been cooled slowly can only be partially dissolved by acids. To obtain a sample which will be decomposed by HCl, the following method has been adopted.

A cast-iron pan, similar to an assay-pan, 5 inches square, and having in it four shallow, hemispherical cups, is riveted to a handle 20 inches long. The cups have the furnace-numbers countersunk in the bottoms. The sample is taken by filling this pan directly, or by means of a ladle, with the fluid-cinder as it flows from the cinder-notch. It chills instantly, and by the time it can be carried to the laboratory, is ready for treatment. By this system, there is no danger of confusion, and there are four small cakes from which to choose a final sample.

Take from 0.2 to 0.5 grms. in a porcelain dish, add strong HCl, heat on a water bath and stir thoroughly

with a platinum wire; when thoroughly mixed, transfer to an iron plate and evaporate to dryness, cool, add 15 c. c. of HCl (1.12 sp. gr.), and boil 2 or 3 minutes to dissolve titanic acid, then add an equal volume of water and filter.

Res. (*a*) = SiO_2.

Filt. (*a*) can be used for estimating Al_2O_3, MgO and CaO.

IRON AND STEEL.

Estimation of Phosphorus.

Take, for analysis, of Bessemer or other low-carbon steels, from 3 to 5 grammes; of crucible steel, 10 grammes; of pig-iron, 1 to 5 grammes, according to the percentage of phosphorus supposed to be present. Of iron, high in phosphorus (1 per cent.), take 1 gramme.

Place in a No. 4 evaporating dish the amount of iron or steel decided upon, cover with a funnel which will just fit inside the dish, and then add gradually HNO_3 (1.20 specific gravity), using 12 c. c. of acid for each gramme of steel or iron taken. (A larger quantity of acid will be required for small samples.) When the full amount of acid has been added, and the violent action has ceased, place the evaporating dish on a sand-bath, add 10 c. c. HNO_3 (1.40 specific gravity), and boil till the bulk of the solution is reduced about one-half. Then add 10 c. c. HNO_3 (1.40 specific gravity), continue the boiling, and add from time to time, during the next 15 minutes, small portions of pulverized $KClO_3$ till about 2 grammes has been added. (If the solution shows signs of going dry, more strong acid must be added.) This will precipitate the manganese, with some iron. Sometimes it happens that the manganese does not come down readily and more $KClO_3$ or further concentration, or both, will be required.

The process is not complete till the manganese is precipitated, which may be known by the appearance

of a dark, mirror-like deposit on the dish, at the edge of the solution.

Boil the solution 5 minutes after the last addition of $KClO_3$, then add cautiously (to prevent sudden explosions) strong HCl till the manganese and iron are dissolved. (From 2 to 5 c. c. will be sufficient, do not use more than 5 c. c. but less if possible.)

Continue the boiling till the chlorine is all expelled, adding from time to time HNO_3 (1.40 specific gravity) to prevent the solution from evaporating to dryness.

Now, add an equal bulk of water to the solution, and boil from 5 to 10 minutes, cool, and filter into a flask. This filtration may be omitted, if, as is generally the case with low-silicon steels, there is no residue.

(X). Place the flask under the hydrant, till the solution is perfectly cold; then add gradually strong ammonia, with constant stirring, till the solution is changed into a pasty mass, and the ammonia is in slight excess; now add cautiously HNO_3 (1.40 sp. gravity) till the mass is dissolved; cool the solution to 60° C., it should then have a straw color. If the solution has a decided red tinge, iron will be thrown down with the phospho-molybdate precipitate, which can only be removed by re-precipitation, and with a loss of phosphorus.

The red tinge can, as a rule, be removed by adding some strong HNO_3, shaking well, and then adding about 25 c. c. of water. (The solution should now not exceed 200 c. c.) Heat to 60° C., and add 60 c. c. of molybdate solution, cork the flask and shake violently for five minutes; place the flask on an iron plate, heated to 60° C. (not more), and let it stand till the precipitate subsides.

By cooling the solution, before adding the molybdate solution, and not raising the heat above 60° C., the phospho-molybdate precipitate is obtained free from molybdic acid, and also, (if the above precautions have been observed), from iron; and will contain only a part of the silica, the whole of the silica being thrown down only by high heat and long standing. Filter through a four inch

filter and wash the precipitate (keeping as much of it in the flask as possible) with the acid solution of ammonium nitrate or with HNO_3 diluted with fifty times its bulk of water; wash till the wash-water will not give a red color with potassium thiocyanate.

Place the flask, which contains the bulk of the precipitate, under the funnel, and dissolve the precipitate of phospho-molybdate on the filter with a 3 per cent. solution of ammonia. The filter should remain perfectly white, or only slightly tinged with red on the upper edge. If much colored with iron, run through the filter into the ammoniacal solution enough dilute nitric acid to dissolve this oxide of iron, and render the solution slightly acid; then add 5 c. c. molybdate solution, heat the flask to 80° C., let it stand 15 minutes or till the precipitate subsides; filter and wash as before. This will give a phospho-molybdate precipitate free from iron. Dissolve this precipitate with a 3 per cent. solution of ammonia, as above.

To the ammoniacal solution of phospho molydate add 5 c. c. strong HCl, or enough to render the solution decidedly acid; dissolve the precipitate thus formed with ammonia, adding it gradually, so that the last drop will just disperse the yellow color, leaving the solution cloudy and with a peculiar sweet smell. Boil the solution 10 minutes; then set it aside till the silica becomes flocculent (about 10 minutes); remove the separated silica by filtering through a small, close filter—or better, through the filter from which the phospho-molybdate precipitate has been dissolved, for the silica is not so liable to pass through that, as through a new filter.

By repeated tests I have been unable to find phosphorus in the separated silica when iron was not present, but have always found it when the silica contained iron. To the filtrate add 5 c. c. of ammonia; cool; and then add gradually 15 c. c. of magnesia mixture, keeping the solution in constant motion; cork the flask and shake violently for two or three minutes; set it aside for three hours; filter and wash with ammonia water (3 parts of

water, 1 part of ammonia) till the wash-water, acidulated with nitric acid, gives no precipitate with silver nitrate.

Place the moist filter with its precipitate in a platinum crucible; cover, and apply a strong heat till the filter is thoroughly charred; remove the cover; turn the crucible on its side, and ignite till the filter is white: then place the crucible in the upright position; cover, and heat five minutes with the blast. This will volatilize the greater part of the molybdic acid, which is nearly always present with the ammonio-magnesium phosphate. The determination may be made in six hours.

$$\text{Result} = Mg_2P_2O_7. \quad 27.93\% = P.$$

Nitric Acid Process.

Take a weighed sample of the steel, and dissolve in HNO_3 (1.20 sp. gr.); add 5 c. c. of HCl, evaporate to dryness and heat on an iron plate to 120° C. until all of the acid is removed; cool, add strong HCl and heat till dissolved, and evaporate cautiously to about 15 c. c., now add 40 c. c. strong HNO_3 and boil down to 15 c. c.: now move the dish about so as to moisten any dry scales that may have formed, when partially cold add 40 c. c. of water (this should give a clear solution) filter and wash. The filtrate should not exceed 150 c. c.

The rest of the operation is conducted as described on page 66 commencing at (X).

E. Fred. Wood's Direct Process.*

Method A. Applicable to iron and steel and manganese-iron alloys.

Weigh 1.63 grm. material into a 4-inch evaporating dish, add 35 c. c. 1.20 HNO_3. Cover with a watch glass, when violent action has ceased put over a lamp and boil down till nearly or quite dry, remove from lamp, and add 15–20 c. c. concentrated HCl, again boil down to dryness, and heat to 200° C. for one hour, or until there is no longer

* Jour. Analyt. Chem. Vol. I, p. 138.

any smell of acid, remove from lamp, cool, add 30–35 c. c. concentrated HCl, boil till all is dissolved except silica and graphite, dilute with a little hot water, filter into 200 c. c. beaker, washing filter with HCl and hot water. (The filtrate and washings need not exceed 125 c. c.) Boil down to 15 c. c., add 35–40 c. c. HNO_3, (sp. gr. 1.42), again boil down to 15 c. c., add 5 c. c. water, cool, add 70 c. c. molybdic acid solution, stir well, let stand at a temperature of 20° to 30° C. for 2 hours, or until the yellow precipitate is completely settled and solution is perfectly clear. Prepare a weighed filter by drying a 6 or 7 cm. filter of Munktell's No. 1 Swedish paper for 35 minutes in steam drying bath at 100° C., weigh rapidly to within 1 milligram. Remove most of supernatant liquor with a siphon, filter remainder, and wash precipitate on a filter with water containing 2 per cent. of 1.20 nitric acid; wash precipitate and filter 4 to 6 times with this mixture, dry at 100° C. for 45 minutes (longer if precipitate is very heavy, the point of the filter should be blue when dried enough) weigh. The yellow phospho-molybdate of ammonia contains 1.63 per cent. phosphorus, so that each milligram = .001 per cent. phosphorus in sample.

Method B. Applicable to steel and wrought iron.

Weigh 1.63 gm. steel into 200 c. c. beaker, add 35 c. c. 1.20 HNO_3 and cover with watch glass, when violent action has ceased, place over lamp and boil till carbonaceous matter is dissolved and solution is concentrated to 15 c. c., add 15 to 20 c. c. chromic acid solution, boil down to 15 c. c., add 5 c. c. water, cool, precipitate and weigh as in method A. For very rapid work nearly as accurate results can be obtained in one hour. When solution is concentrated after adding chromic acid solution, rince into Erlenmeyer flask using as little water as possible (not over 8 c. c.), cool to 30° C., add 70 c. c. molybdic acid solution, previously warmed to 30° C., cork and shake violently for five minutes, let stand 10 minutes, when precipitation will be complete. Filter through weighed

filter, wash, dry 15 minutes at 135° C. This method was tried in pig iron, but the concentrated HNO_3 precipitated silica in such a form that it could not be filtered. This difficulty was avoided in

Method C. Applicable to pig irons.

Place 1.63 gm. in a 200 c. c. beaker, add 35 c. c. 1.20 HNO_3, boil 3 or 4 minutes, add 3 to 5 drops hydrofluoric acid and 15 c. c. water, boil down to 15 c. c., add 18 c. c. chromic acid solution, boil 5 minutes. Filter through asbestos filter, wash filter with hot water, concentrate filtrate to 20 c. c., cool and precipitate. Time required about 2½ hours. As yet satisfactory results have not been obtained on ferromanganese, though the method works well on white iron and spiegel up to 20 per cent. manganese.

SPECIAL REAGENTS.

Chromic Acid Solution.—Dissolve about 50 gms. CrO_3 in 1 liter 1.42 nitric acid, by warming. The solution should be renewed occasionally as it seems to lose oxydizing power on standing 3 or 4 weeks.

Filter Paper.—The best paper for filtering off silica and graphite in method A was found to be Schleicher and Schüll's No. 597, about 9 cm. diameter filter being used. For collecting and weighing the phospho-molybdate the most suitable paper found was J. C. Munktell's No. 1 Swedish.

Volumetric Method of Estimating Phosphorus.

The accuracy of this method will depend upon the composition of the phosphomolybdate precipitate being constant. To test this, I have made many estimations; and the precipitates obtained from known quantities of phosphorus agreed with each other, and corresponded with the following well known formula when the precipitation took place at 60° C. or less.

$$3(NH_4)_2O.\ P_2O_5.\ 22MoO_3.\ 12H_2O.$$

This formula contains 1.6838 per cent. of phosphorus, and 86.04 per cent. MoO_3.

The volumetric method is based upon the fact, that, the MoO_3 in the phosphomolybdate precipitate can be reduced to Mo_2O_3 by zinc and dilute sulphuric acid; and the Mo_2O_3 thus formed can be oxidized to MoO_3 by titrating the solution with potassium permanganate. The following reaction takes place in this titration: $5Mo_2O_3 + 6KMnO_4 + 9H_2SO_4 = 10MoO_3 + 3K_2SO_4 + 6MnSO_4 + 9H_2O$. From this reaction we obtain the $\frac{N}{10}$ factor of MoO_3, as follows:

$6KMnO_4$ oxidizes $5Mo_2O_3$ to 10 MoO_3

Therefore, $KMnO_4 = \frac{10}{6}$ MoO_3; or by substituting the atomic weights, 158 = 240.; and by dividing by 5 we have 31.6 = 48.

$\frac{N}{10}$ factor of $KMnO_4$ = .00316
$\frac{N}{10}$ " " MoO_3 = .0048

From the foregoing data, we obtain the $\frac{N}{10}$ factor of phosphorus by this simple proportion:

86.04 (MoO_3) : 1.6838 (P) : : 0.0048 ($\frac{N}{10}$ factor of MoO_3) : x = 0.0000939 ($\frac{N}{10}$ factor of P) or 0.000094.

This factor, thus obtained by calculation, has been verified by analysis.

The first results obtained were not constant, and were too high, due to the varying amounts of zinc sulphate present, which is formed in reducing the MoO_3; for I have found that pure zinc sulphate as well as that formed in reducing the MoO_3 to Mo_2O_3, will reduce potassium permanganate. It is therefore necessary to first ascertain the reducing power of the zinc sulphate which is formed in the first part of this operation, which may be determined as follows:

Take 10 grms. of Zn, add 75 c. c. of water then 15 c. c. of strong H_2SO_4, when violent action has ceased, heat so as to maintain a rapid evolution of hydrogen during 15 minutes, filter, to the filtrate add 2 c. c. of H_2SO_4, cool

under the hydrant to 30° or 40° C., and titrate with $\frac{N}{10}$ $KMnO_4$ to a permanent pink color. Deduct the c. c. of $KMnO_4$ used from each titration of the phosphomolybdate precipitate. (This reducing power of zinc sulphate varies with the zinc used, but is constant for the same zinc).

Reduction and Titration of the Phosphomolybdate Precipitate.—After washing the precipitate in the usual manner, it must be washed twice with pure water to remove the nitric acid; then dissolve in dilute ammonia, and dilute the solution to 150 c. c. with water, divide into two equal portions and to each add 10 grms. of the tested Zn and 15 c. c. of strong H_2SO_4, cover, and apply heat to maintain a rapid evolution of hydrogen for 15 minutes, now filter as rapidly as possible allowing the undissolved zinc to go on to the filter, rinse out the flasks several times with dilute H_2SO_4, then fill the filters once with cold water, and as soon as this has passed through, cool the solutions under the hydrant and titrate each as rapidly as possible with $\frac{N}{10}$ $KMnO_4$ till a faint, permanent, pink color is produced. The solution after reduction is dark, which on titration grows lighter till it becomes perfectly white, then a few more drops of $KMnO_4$ will produce the pink color.

Estimation of Silicon.

Dissolve 0.5 grm. in 20 c. c. of dilute sulphuric acid (1 pt. H_2SO_4 to 8 pts. water) in a porcelain evaporating dish When dissolved add 1 c. c. of HNO_3 (1.40 sp. gr.), and 2 c. c. of strong H_2SO_4 and evaporate until white fumes of SO_3 are given off, continue the heat 5 or 10 minutes; then cool, add some strong HCl, then 10 c. c. of water, and heat until dissolved; filter, wash with hot water containing 5 per cent .of HNO_3. Residue = SiO_2.

In estimating silicon in ferro-manganese and spiegel, it is necessary to dissolve in HNO_3 (1.40 sp. gr.), then add H_2SO_4 and proceed as above.

Estimation of Sulphur.

First Method.

Take from 3 to 5 grms., place in a generating flask, which has a funnel-tube with a stop-cock, connect the flask with three small, three-bulb U-tubes; fill these tubes one-third full with a solution of $KMnO_4$ (1 grm. $KMnO_4$ to 200 c. c. water). The $KMnO_4$ must be free from sulphuric acid. Now, gradually let into the generating flask dilute HCl (1 pt. HCl to 2 pts. water). The HCl must be free from Cl. A rapid evolution of gas must be avoided. Continue the operation until all of the iron is dissolved, then heat the flask nearly to boiling, and draw air through for some time. Empty the U-tubes into a beaker, rinse first with water, then with strong HCl to dissolve the oxide of manganese adhering to the sides. Now add about 15 c. c. of strong HCl and evaporate rapidly; after the solution has been reduced to about one half of its original bulk, if it is not clear add more HCl and continue the boiling until a clear solution is obtained; that is until the $KMnO_4$ has all been reduced. Neutralize the excess of HCl with ammonia and precipitate the sulphuric acid in the usual manner.

If this last solution contains a sediment, on account of impurities in the $KMnO_4$, then filter before precipitation.

If the whole amount of sulphur is to be saved, then the residue in the generating flask must be filtered out, digested with aqua regia twice, and evaporated to dryness each time, then taken up with HCl and water, filtered, and the filtrate added to the above solution before precipitation with $BaCl_2$.

Second Method.

Proceed according to directions given above, using in the U-tubes in place of $KMnO_4$, a solution of caustic soda (1 pt. NaHO to 5 pts. water). This solution of soda must be free from sulphur, or its compounds, or

any agent which will reduce iodine. Empty the U-tubes into a large flask, rinse well with water, and dilute to 200 or 300 c. c., acidify with strong HCl (free from Cl), add starch solution, and titrate with $\frac{N}{100}$ solution of iodine.

$\frac{N}{100}$ factor of S = .00016.

Third Method.

Cadmium Solution. Take 250 grms. of CdCl, dissolve it in water, and add enough NH_4OH to dissolve the precipitate which may form, then heat and filter, if necessary, and dilute to four litres with strong NH_4OH.

Take 15 c. c. of this solution, dilute it with 150 c. c. of water, if a precipitate forms add some NH_4OH to dissolve it. Now take 5 grms of iron in a generating flask and dissolve it with dilute HCl (1 of acid to 2 of water) and pass the gas into this last solution of CdCl. When the iron is all dissolved, dilute the cadmium solution with water to 400 c. c. then add gradually dilute HCl till the solution is acid; now titrate with standard iodine.

The sulphur in the residue may be estimated as directed in the *first method.*

If perfectly accurate results are desired the cadmium sulphide must be filtered off and then removed from the filter and titrated; for the cadmium solution which destroys iodine, absorbs carburetted-hydrogen, thus giving too high a per cent of sulphur.

Estimation of Manganese.

GENERAL METHOD FOR PRECIPITATING THE MANGANESE AS MnO_2 BY HNO_3 AND $KClO_3$.

Take of pig-iron from 2 to 5 grms., dissolve in HNO_3 (1.2 sp. gr.), using 12 c. c. of the acid for each grm. of iron taken, filter, evaporate the filtrate to a pasty condition, and then add 40 c. c. HNO_3, (1.40 sp. gr.). Take of steel 2 grms., dissolve in 25 c. c. of HNO_3 (1.20 sp. gr.) and evaporate to a pasty condition, then add 40 c. c. of HNO_3 (1.40

sp. gr.). Take of spiegel 0.5 grm., or of ferro 0.1 grm., dissolve in 40 c. c. of HNO_3 (1.40 sp. gr.).

Use a pint beaker for dissolving the iron or steel, and a 12 oz. beaker for spiegel or ferro.

Boil the solution thus prepared, and while boiling add 2 grms. of pulverized $KClO_3$, in small quantities at a time; this need not take more than five minutes.

Now add 20 c. c. of HNO_3 (1.40 sp. gr.), boil and add a little more $KClO_3$ (about 0.1 grm.), boil 5 minutes after the last portion of $KClO_3$ has been added, then remove from the lamp and cool. Filter through purified asbestos, suck the filter dry with the aspirator, then wash with purified HNO_3 (1.40 sp. gr.) until the acid comes through clear, again suck dry with the aspirator.

Pp (*a*) = MnO_2 + Fe_2O_3 with some nitric acid.

GRAVIMETRIC METHOD.

Transfer *Pp* (*a*) with the asbestos to the beaker in which the precipitate was formed, add HCl and boil until the MnO_2 is all dissolved; filter and wash with hot water. The filtrate contains some iron with the manganese; nearly neutralize with ammonia, add a very small lump of sodium acetate, and boil; filter, wash slightly with hot water, redissolve the precipitate in HCl, and reprecipitate the iron; unite the two filtrates, heat nearly to boiling, add an excess of sodium ammonium phosphate, then ammonia in slight excess and boil till the precipitate presents a silky appearance. Filter, dry, ignite and weigh.

Result = $Mn_2P_2O_7$. Wt. of $Mn_2P_2O_7 \times .3873$ = Wt. of Mn.

VOLUMETRIC METHOD.

No. 1.

Transfer *Pp* (*a*) with the asbestos to the beaker in which the precipitate was formed, add about 75 c. c. of water and then run in $\frac{N}{10}$ ammonio-ferrous sulphate (made by dissolving 39.2 grms. of the salt in water, adding 50 c. c. of strong H_2SO_4 and diluting to one litre, when

cold), 5 c. c. at a time, stirring thoroughly after each addition, until the MnO_2 is all dissolved. (Do not heat). A weighed amount of the salt and H_2SO_4 may be added instead of the $\frac{N}{10}$ solution. Now titrate back the excess of ammonio-ferrous sulphate with $\frac{N}{10}$ $KMnO_4$, the first flash of the rose color is the end reaction; deduct from the $KMnO_4$ used 0.2 c. c. If in doubt about the end reaction, place a few drops of freshly prepared ferricyanide of potassium on a porcelain plate, and test the solution with it, titrating back and forth with $\frac{N}{10}$ ammonio-ferrous sulphate, and $\frac{N}{10}$ $KMnO_4$, until a satisfactory end reaction is obtained.

Multiply the number of c. c. of $\frac{N}{10}$ ammonio-ferrous sulphate actually used by .00275 the $\frac{N}{10}$ factor of Mn.

VOLHARD'S VOLUMETRIC PROCESS.

No. 2.

This process is based upon the following reaction which takes place in titrating manganous sulphate with potassium permanganate.

$$3MnSO_4 + 2H_2O + 2KMnO_4 = 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

$\frac{N}{10}$ factor of Mn = .00165.

Take 2 grms. of steel (more or less according to the per cent, of Mn), place it in a porcelain dish, add 10 c. c. of strong H_2SO_4, and 40 c. c. of HNO_3 (1.20 sp. gr.); when dissolved boil on a sand bath until white fumes of SO_3 are given off, continue the boiling two minutes longer. Cool, dissolve in hot water, transfer to a large flask graduated to hold 500 c. c., (The dilution must be 250 c. c. for each grm. of iron taken) add dry sodium carbonate till the solution turns red, then add an excess of the oxide of zinc paste, shake well, and as soon as the acid is all neutralized the precipitate will settle readily; dilute to the mark with cold water and shake well. Filter through a large, dry, plaited filter; take 100 c. c. of the filtrate, place it in a 250 c. c. flask, add 20 c. c. of the solution of zinc phate, boil, and titrate with $\frac{N}{10}$ $KMnO_4$. In titrating

shake the flask violently after each addition, and reheat toward the last. The end reaction is the production of a faint permanent rose color.

VOLUMETRIC PROCESS.

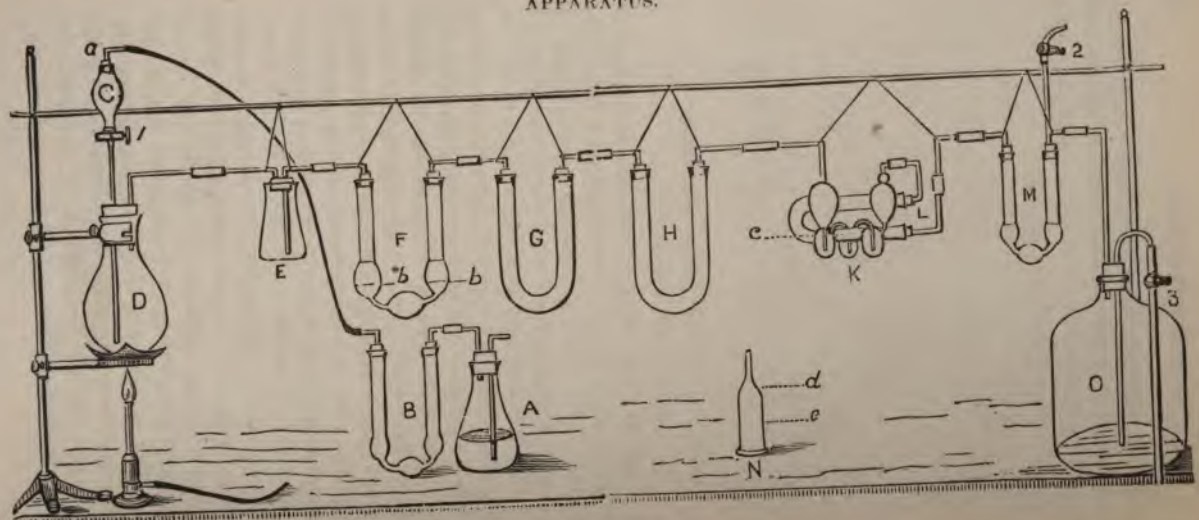
No. 3.

Take 2 grms. of steel, dissolve in 30 c. c. of 1.20 HNO_3, when dissolved boil for 5 minutes, dilute with water, transfer to a 500 c. c. flask, add dry sodium carbonate till the solution turns red, then add an excess of oxide of zinc paste, dilute to the mark with cold water, shake well, and filter through a large, dry, plaited filter. Take 200 c. c. of the filtrate, add some of the oxide of zinc paste, heat rapidly till the solution boils, and titrate with $\frac{N}{10}$ $KMnO_4$. $\frac{N}{10}$ factor of Mn = .00165.

Estimation of Total Carbon.

[See Illustration on Page 78.]

A and B are for removing CO_2 from the air; A is filled one-third full with a solution of KHO, and B is filled with soda-lime. C is a funnel tube for transmitting the solutions into the generating flask D; it is connected by a rubber tube, and cork (a) with the U-tube B, so that all the air which enters the apparatus at this end is freed from CO_2; it is also provided with a stop-cock. D is the generating flask. E is a flask for condensing any vapor that may pass over during the operation; the bottom is covered with strong H_2SO_4; the entrance tube passes just through the cork and the exit tube extends down to within one-quarter of an inch of the H_2SO_4; the flask must be immersed in a beaker of cold water. F is an eight inch, three bulb U-tube, filled to the mark (b) with strong H_2SO_4. G is an eight inch, straight U-tube, filled with granular calcium chloride. H is an eight inch straight U-tube, the left arm filled with anhydrous copper sulphate, and the right arm with granular calcium chloride. K is a potash bulb filled to the mark (c) with KHO (1.27 sp. gr.); there is connected with, and fastened to it, a four inch, straight U-tube L, the upper arm filled



See Page 77.

with soda-lime, and the lower arm with granular calcium chloride. K and L are for the absorption of the carbon dioxide. M is its guard tube, the left arm filled with granular calcium chloride, and the right with soda-lime. O is an aspirator bottle, which holds five litres of water. N is a funnel for collecting the carbon.

If the corks and rubber tubing are new, boil in a solution of CrO_3 in H_2SO_4 and wash thoroughly before use.

The combustion should be made in a room as free as possible from acid fumes, and blank tests should be made and the guard tubes increased till a constant weight of the potash bulb is obtained.

Dissolving the Iron or Steel.—Weigh out 3 grms. of the fine iron or steel, add 200 c.c. of the double chloride of copper and ammonium solution, stir the solution frequently, and after a few minutes apply a gentle heat (50° or 60° C.). When the iron and the precipitated copper have been dissolved, add a few drops of HCl to dissolve the thin film of oxide of iron which has formed on the surface. The carbon is now collected in the funnel N, which is *loosely* stopped with a small quantity of purified asbestos. Hot water is first run through the filter, then the solution; the residue is washed once with the double chloride, and then with hot water, until the wash water gives, with $AgNO_3$, no test for chlorine. The funnel is then broken into three pieces, by scratching at d and e with a file and applying a hot iron; the pieces, with the carbonaceous residue, are next introduced into flask D. The whole apparatus is now carefully connected, and the aspirator set running, valves 1 and 3 being open and 2 closed; and one litre of air drawn through; now close valve 3 and open valve 2. After standing thirty minutes disconnect K and L and weigh them. Re-connect K and L, close valves 1 and 2, remove the cork (a) and by means of a funnel introduce into C, 90 c.c. of the solution of CrO_3 and H_2SO_4. (The amount to be used of this solution will depend upon the carbon present. For 3 grms. of steel with one per cent. of carbon or less, use 90 c.c. For

pig iron, or high carbon, use at least twice this amount, or take less of the metal in order to maintain about the same ratio between the carbon and oxidizing reagent). Then insert cork (a) and open valve 3, and as soon as air bubbles commence coming through K, open valve 1 and allow the solution to flow gradually into D. Now close valve 1 and apply heat to D; shake D carefully to insure thorough contact of its contents, and continue the heat till white fumes appear, or, to incipient ebullition. Remove the lamp and gradually open valve 1 till wide open, when the aspirator O is half empty, open valve 3 so that the air bubbles will come over more rapidly. At first the bubbles should not come through faster than three in a second, and at no time fast enough to throw the potash solution in K into the exit tube. When the aspirator O is nearly empty close valve 3, and in about five minutes open valve 2; allow the apparatus to stand thirty minutes, then disconnect K and L and weigh them; the increase of weight is the weight of CO_2, of which 27.3 % is C.

Estimation of Graphite.

Take about 2 grms. of iron, add an excess of HCl (1.12 sp. gr.), heat moderately until no more gas is evolved, filter through purified asbestos, wash with hot water, then with a solution of potash, next with alcohol, and lastly with ether; dry thoroughly and oxidize with CrO_3.

Colorimetric Determination of Combined Carbon.

Select for color standards, steels, which are as nearly like the samples to be treated as possible, both as to chemical composition and mechanical treatment, and treat the standards and samples to be tested exactly alike in working.

A widely varying chemical composition in other elements than carbon and iron, and the mechanical treat-

ment, as well as the varying modes of carrying on the analysis, all make differences in the intensity and shade of color given by combined carbon in steel to its nitric acid solution.

The mechanical state of division of the standard and samples to be treated must be about the same.

Drillings are generally used, since they are less liable to contain foreign matter, and as a rule, are sufficiently coarse to prevent too rapid solution.

One-tenth of a grm. is usually taken, although varying amounts up to five-tenths are used.

I prefer to take one-tenth of a grm. as being more convenient to work with, although the error is slightly less with a greater weight.

The amount of nitric acid (1.20 sp. gr.) to be used will depend upon the per cent. of carbon as well as upon the amount of steel taken. For 0.1 grm. of steel, with carbon from 0.00 per cent. up to 0.50 per cent. use 3 c. c. of acid; from 0.50 up to 1.00 per cent. carbon use 4 c. c.; from 1.00 up to 1.75 per cent. of carbon use 5 c. c.; above 1.75 per cent. of carbon use 8 c. c.

Place the weighed samples in 5 inch test tubes, and immerse them in cold water, then run into each tube, gradually, 3 c. c. of HNO_3 (1.20 sp. gr.) for each 0.1 grm. of steel taken. (The nitric acid must be free from chlorine, nitrous fumes, and organic matter.) Allow them to stand until all action has ceased in the cold.

The samples under examination are now compared with the standard by removing the tubes successively from the water, and more acid is added to the darker samples if it is deemed necessary. The cold water in which the tubes are immersed is now rapidly brought to boiling, and boiled for fifteen minutes if the steel has less than 0.15 per cent. carbon, for twenty minutes if between 0.15 and 0.30, and for thirty minutes if between 0.30 and 0.80, and for forty-five minutes if above 0.80 per cent. carbon.

If the solution becomes turbid, due to a deposit of

nitric acid and oxide of iron, then the sample should not be heated above 70° C.

The test tubes should be shaken several times during the boiling, which should be performed in a moderately dark room or closet, and the water in the bath should be kept at least on a level with the solutions in the tubes, which can be accomplished by adding from time to time *boiling* water to the bath.

After the boiling, remove the test tubes from the bath and plunge them into cold water, and, when cold, place them in a rack and exclude the light, then add to each tube 3 c. c. of water for each 0.1 grm. of steel taken, which will destroy the tint of oxide of iron. Shake the tubes, and if there is any graphite present filter through a very small *dry* filter.

When placing the tubes in the rack after cooling, arrange them according to the depth of color, the darkest one at one extremity and the lightest at the other.

For comparing the colors use a pair of graduated tubes, with $\frac{3}{8}$ or $\frac{1}{2}$ inch internal diameter; these tubes must be made of colorless glass, must have the same internal bore and thickness of glass walls, and must be calibrated.

In matching the colors use a camera-shaped box, painted black inside, with two holes through the upper part near the small end for inserting the tubes, and with a piece of pure, white filter-paper fastened over the small end.

Take the test tube containing the standard and compare it with the rack of samples, and select the one which has the same or a slightly darker color, as the beginning point. Transfer the standard to one of the graduated tubes, and dilute it with water so that 1 c. c. represents 0.1 or 0.05 per cent. of carbon. If we take 0.1 grm. of a 0.30 per cent. carbon steel, and after dissolving dilute it to 6 c. c., each c. c. represents 0.05 per cent. of carbon ($0.30 \div 6 = 0.05$). If our standard is a 0.31 per cent. carbon, then we must dilute it to 6.2 c. c. ($0.31 \div 6.2 = 0.05$).

Having thus diluted the standard, take the other graduated tube and empty into it the test-tube which has been selected as the beginning point, place the two in the camera box, and if the sample under examination is darker than the standard, dilute it with water until it has the same color as the standard; note the number of c. c. and multiply them by 0.05; this gives the per cent. of carbon. Compare all the darker samples in the same manner. Now dilute the standard with an equal volume of water, then each c. c. represents 0.025 per cent. of carbon, and compare the lighter colors with it in the same manner.

TITANIC IRON.

Estimation of Silica, Titanium, and Iron.

Fuse in a platinum crucible enough $KHSO_4$ to form in the bottom a mass, one-quarter of an inch thick. Weigh 0.2 grms. of the ore, mix it thoroughly with 3 grms. of the finely pulverized, fused $KHSO_4$ and charge it into the crucible, and place on top of all some fine, fused $KHSO_4$, cover the crucible, and heat very moderately for five minutes. (The heat must be just sufficient to expel a very small amount of SO_3). Now increase the flame, and so place the crucible that the bottom will be in the cool part of the flame (that is, two or three inches from the burner, according to the size of the flame), continue this heat five minutes, then remove the lamp, and examine the charge. It will be fluid, and one can readily see whether or not the ore is all fused. If not, heat a little longer, and add more fused $KHSO_4$ if necessary.

When fused, allow it to cool till it begins to solidify, then pour into a hot porcelain evaporating dish as much of it as possible, place the crucible in the dish, and when cold dissolve in cold water and filter.

Res. (*a*) = Silica and calcium sulphate. While yet moist wash the residue with a saturated solution of sodium

hyposulphite, which will dissolve the calcium sulphate, and finally with distilled water to remove the hyposulphite. This wash water must not be added to filt. (a).

Filt. (*a*) contains the titanic acid, the iron and some lime. Dilute to 500 c. c., add a few drops of nitric acid to prevent the ferric iron from coming down with the titanic acid and boil for some time, maintaining the bulk of the solution by adding from time to time hot water. Filter.*

Pp. (*b*) = TiO_2. Dry and ignite, cool, add a little dry ammonium carbonate, and again ignite to expel any sulphuric acid that may be present.

Filt. (*b*) contains the iron and part of the lime; add to it the wash water from res. (a), and then determine the total iron, and the lime.

CHROME IRON ORE.

Estimation of Cr_2O_3.

Take 0.5 grm. of the very finely pulverized ore and mix it with 6 grms. of fused $KHSO_4$ in a large platinum crucible, fuse for 15 minutes at as low a heat as possible, then raise the heat gradually till the full heat of the Bunsen burner has been attained; now apply the blast and heat for 15 minutes longer; cool, add 3 grms. of dry sodium carbonate, fuse, and project into the fused mass, from time to time, potassium nitrate till about 3 grms. have been added. This last fusion will require about one hour. The whole operation must be carefully watched from the first and the contents of the crucible not allowed to run over the sides. Dissolve the fused mass in boiling water, filter while hot, and wash with hot water = filt. (a).

Res. (*a*). Digest with HCl for three hours; if a dark residue remains, filter, throw away the filtrate, and fuse the residue as above, and add the filtrate to filtrate (a).

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*Crookes 197.

Filt. (*a*). Add an excess of ammonium nitrate, evaporate on a water bath, nearly to dryness, or until all of the liberated ammonia has been expelled, then add water and filter.

Filt. (*b*). Add a few drops of H_2SO_4 and then a small piece of bisulphite of soda, and boil till all the CrO_3 is reduced to Cr_2O_3 and the excess of sulphurous acid has been expelled, (the solution will be bright green). Now add ammonia in slight excess and boil till the excess is expelled, filter and wash with hot water. The filtrate should be colorless.

LEAD SLAGS.

Proximate Analysis.

The silver and lead are generally estimated in the dry way.

Estimation of Silica.—Dissolve a weighed sample (1 grm.) in strong HCl, add some HNO_3 to oxidize the iron, evaporate to dryness, take up with HCl and water, filter and wash by decantation with boiling water. The residue of silica, with some foreign matter, is ignited in the usual way. The filtrate can be used to estimate alumina, iron, lime, and magnesia (see Blast Furnace Slag).

Estimation of Iron.—Dissolve 1 grm. of the slag in strong HCl, and filter; if copper is present it must be removed; now titrate the iron with stannous chloride and $\frac{N}{10}$ $K_2Cr_2O_7$.

Estimation of Manganese.—Dissolve a weighed sample in HCl, add enough HNO_3 to oxidize the iron, then add a moderate excess of H_2SO_4 and evaporate till white fumes (SO_3) are given off; cool, dilute with water, and filter; titrate the filtrate with $\frac{N}{10}$ $KMnO_4$.

Estimation of Lime.—Dissolve 0.5 grm. of the slag in aqua regia, and filter; add to the filtrate ammonia in slight excess, and boil; continue the boiling and add gradually

a saturated solution of oxalic acid until the iron is dissolved, then add ammonia till a slight precipitate of iron is formed, now add very cautiously more oxalic acid until the iron is dissolved, boil for fifteen minutes after the last addition of oxalic acid, and then filter. (If iron is precipitated with the lime, dissolve in HCl and reprecipitate.) Titrate the precipitate for lime according to directions given.

COPPER ORES AND PRODUCTS.

Estimation of Copper by the Battery.

A method for estimating copper in all ores and substances, which do not contain elements that are precipitated by the battery from acid solutions.

Take 2 grms. if the ore carries more than 10 per cent. of copper, add 5 c. c. of strong H_2SO_4, then a little HNO_3 from time to time until action ceases; heat on a sand bath until white fumes appear, and the mass is nearly dry; cool, add 30 c. c. of water, boil and filter, wash with water acidulated with H_2SO_4 (if there remains a black residue treat it as before). Place the filtrate, or a part of it, in a weighed platinum dish, then place the dish in the circuit of a moderately strong battery;* when the solution has lost its color, test a drop of it with H_2S water; if any copper remains in the solution, a dark precipitate will be formed. Wash the precipitated copper two or three times with hot water, then with alcohol; ignite the remaining alcohol and when burnt off, weigh; if the copper solution is too strong the copper will not all adhere to the dish, but will appear as loose, granular copper; this will also happen if the current of the battery is too strong.

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* By using two Bunsen elements and heating the copper solution to 70° or 80° C., the copper will be precipitated in four hours. (Classen on electrolysis 65.)

Estimation of Copper by Potassium Cyanide.

Dissolve the sample as in the preceding method, and filter into a large beaker, in which has been placed a rod of zinc to which has been fastened a strip of platinum foil. When the copper is all precipitated, remove the zinc, and wash the copper by decantation, using a little sulphuric acid in the wash water. Dissolve the copper in the least quantity of nitric acid possible, add about 50 c. c. of water, then add NH_4OH till the precipitate which first forms is just dissolved, now dilute to a given number of c. c. and titrate with standard Potassium Cyanide.

ZINC ORES.

Estimation of Zinc.

For rich ores take 0.5 grm., for poor ores 1 to 2 grms. Dissolve the ore in aqua regia, evaporate to dryness, and treat the residue with HCl and water. Pass into this strongly acid solution H_2S gas and filter.

Pp. (*a*) = CuS, etc.

Filt. (*a*). Boil and add a few crystals of $KClO_3$ to oxidize the sulphur and iron, continue the boiling until the odor of Cl has disappeared; cool, and add NH_4OH in slight excess, boil, and filter. If there is much iron, dissolve the precipitate in HCl and reprecipitate with ammonia, and filter. Unite the filtrates.

Pp. (*b*) = Fe_2O_3, etc.

Filt. (*b*). Neutralize with HCl, and then add 15 c. c. more of HCl, and dilute to 200 or 300 c. c. Take 30 to 50 c. c. of this solution, heat nearly to boiling, add a few drops of a solution of uranium acetate, and titrate with the standard solution of Potassium Ferrocyanide.

While the above is for the estimation of zinc only, it can be used for estimating copper and zinc in certain ores

and lead furnace slags. For this purpose take *Pp.* (*a*), dissolve in HCl, boil and add a few crystals of $KClO_3$ and continue the boiling till the odor of chlorine disappears; filter, and add to the filtrate NH_4OH and titrate with Potassium Cyanide as directed under copper ores and products.

ARSENIC ORES AND PRODUCTS.

Estimation of Arsenic.

Take 0.5 grm. of the very fine ore, and fuse it, in a large porcelain crucible, with from 6 to 10 times its weight, of a mixture of equal parts of Na_2CO_3 and KNO_3. Apply a moderate heat at first, and near the top of the crucible if possible. When thoroughly fused and no more bubbles escape, cool, and dissolve in hot water. Filter and acidulate the filtrate with HNO_3, and boil till CO_2 is all expelled; cool and exactly neutralize with NH_4OH. If a precipitate is formed (alumina, etc.), filter it off. Add to this solution silver nitrate in excess, stir well, then add from a burette (a drop at a time) a dilute solution of NH_4OH (1 part NH_4OH to ten parts water) till neutral, or slightly alkaline; stir thoroughly. The arsenic will be precipitated as the brick-red arsenate of silver (Ag_3AsO_4). Filter and wash the precipitate with cold water. Dissolve the precipitate on the filter with dilute HNO_3, add to this solution a few drops of ferric nitrate, and titrate with $\frac{N}{10}$ Ammonium Sulphocyanate.

Each c. c. = .0025 As.

If the ore carries a large per cent. of arsenic, first digest it with strong HNO_3, evaporate to dryness, and then add the fusing mixture and fuse as given above.

MANGANESE ORES.

Technical Examination of Manganese Ores used for Bleaching Purposes.

Pulverize 2 or 3 grms. very fine and dry at 120° C. in an air bath. Weigh out about 0.5 grm., place in a 250 c. c. flask and add 6 grms. of crystalized ammonio-ferrous sulphate, and about 20 c. c. of water, warm till the salt is dissolved, then add strong H_2SO_4 and heat till the ore is completely decomposed. Now titrate the excess of the double iron salt with $\frac{N}{10}$ $K_2Cr_2O_7$, and multiply the c. c. of $\frac{N}{10}$ $K_2Cr_2O_7$ required by .0392; the product will be the number of grms. of the double iron salt undecomposed.* Deducting this amount from the grms. taken we will have the grms. of the double iron salt that have been oxidized, which multiplied by 0.111 will give the amount of peroxide of manganese in the weight taken.

INSOLUBLE SILICATES.

Estimation of Potash and Soda in Feldspar, Etc.

Take 0.5 grm. of the finely pulverized silicate and mix it with 0.5 grm., or a little more, of NH_4Cl in an agate mortar; then add 4 grms. of carbonate of lime in three portions, mixing intimately after each addition. Charge this mixture into a platinum crucible. Place the crucible in an inclined position on the triangle and apply a gentle heat (commencing at the top and gradually carrying it toward the bottom) until the NH_4Cl is completely decom-

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*If $\frac{N}{10}$ $KMnO_4$ is used, the end reaction must be determined by using potassium ferricyanide as in titrating with $K_2Cr_2O_7$; for I have found that solutions containing a considerable quantity of sulphate of manganese will reduce $KMnO_4$, and the rose color will not be obtained till long after the ferrous iron has all been oxidized, if at all.

posed. This will take from 5 to 10 minutes. Now plac the crucible in the upright position, and apply a brigh red heat for from 40 to 60 minutes. Cool the crucible when cold the contents will be found to be a semi-fuse mass; place in an evaporating dish, add water, and hea till the mass slakes; remove the crucible, washing it thor oughly with water, and digest the mass one hour longe or till completely disintegrated. Filter and wash well The filtrate contains all the alkalies of the mineral, an some calcium chloride and caustic lime; add some ammo nium carbonate, and concentrate to about 50 c. c.; the add a little more ammonium carbonate and a few drop of ammonia, and filter; to this filtrate add a few drops o ammonium carbonate, and concentrate; if a precipitate i formed, filter it off and repeat the last operation till precipitate ceases to be formed; now evaporate to drynes in a weighed platinum dish on a water bath; when dry heat, at first moderately, over the Bunsen burner unti the NH_4Cl is driven off, and then gradually increase th heat to faint redness; cool, and weigh. This weight i the chlorides of the alkalies, or the weight of mixe chlorides.

Indirect Determination of the Potash and Soda in th Mixed Chlorides.—Dissolve the mixed chlorides in wate and determine by titration with $\frac{N}{10}$ $AgNO_3$ the tota chlorine: Then by means of the following formulæ th quantities of NaCl and KCl are determined.

W = weight of mixed chloride.
C = weight of chlorine.
$NaCl = C \times 7.6311 - W \times 3.6288.$
$KCl = W \times 4.6288 - C \times 7.6311.$

SUPERPHOSPHATES.

Method for Determining Phosphoric Acid and Moisture.

PREPARATION OF REAGENTS.

(1) *To prepare ammonium citrate solution.*—Mix 370 grams of commercial citric acid with 1,500 cubic centimeters of water; nearly neutralize with crushed commercial carbonate of ammonia; heat to expel the carbonic acid; cool; add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline) and bring to volume of two litres. Test the gravity, which should be 1.09 at 20°, before using.

(2) *To prepare molybdic solution.*—Dissolve 100 grams of molybdic acid in 400 grams or 417 cubic centimeters of ammonic of specific gravity 0.96, and pour the solution thus obtained into 1,500 grams or 1,250 cubic centimeters of nitric acid of specific gravity 1.20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phospho-molybdate. Decant the solution from any sediment, and preserve in glass-stoppered vessels.

(3) *To prepare ammonium nitrate solution.*—Dissolve 200 grams of commercial ammonium nitrate in water and bring to a volume of two liters.

(4) *To prepare magnesia mixture.*—Dissolve 22 grams of recently-ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid, filter, add 280 grams of ammonium chloride, 700 cubic centimeters of ammonia of specific gravity 0.96, and water enough to make the volume of two liters. Instead of the solution of 22 grams of calcined magnesia 110 grams of crystallized magnesium chloride ($MgCl_2$, $6H_2O$) may be used.

(5) *Dilute ammonia for washing.*—One volume ammonia of specific gravity 0.96 mixed with three volumes

of water, or usually 1 volume of concentrated ammonia with 6 volumes of water.

(1) *Preparation of sample.*—The sample should be well intermixed and properly prepared, so that separate portions shall accurately represent the substance under examination, without loss or gain of moisture.

(2) *Determination of moisture.*—(*a*) In potash salts, nitrate of soda, and sulphate of ammonia heat 1 to 5 grams at 130° C. till the weight is constant, and reckon water from the loss. (*b*) In all other fertilizers heat 2 grams, or if the sample is too coarse to secure uniform lots of 2 grams each, 5 grams for five hours at 100° in a steam bath.

(3) *Water-soluble phosphoric acid.*—Bring 2 grams on a filter, add a little water, let is run out before adding more water, and repeat this treatment cautiously until no phosphate is likely to precipitate in the filter. If the washings show turbidity after passing the filter clear up with acid. When the substance is nearly washed in this manner it is transferred to a mortar and rubbed with a rubber tipped pestle to homogeneous paste (but not further pulverized), then returned to the filter and washed with water until the filtrate measures not less than 250 cubic centimeters. Mix the washings. Take an aliquot (usually corresponding to ½ gram of the substance) and determine phosphoric acid, as under total phosphoric acid.

(4) *Citrate-insoluble phosphoric acid.*—Wash the residue of the treatment with water into a 150 cubic centimeter flask with 100 cubic centimeters of strictly neutral ammonium citrate solution of 1.09 density, shred and add the filter paper, cork the flask securely, place in a water bath with constant temperature of 65° C., and digest for thirty minutes at this temperature with frequent shaking, filter the warm solution quickly and wash with water of ordinary temperature. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10 to 15 cubic centimeters of concentrated hydrochoric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 cubic centimeters,

mix, pass through a dry filter, take an aliquot and determine phosphoric acid as under total.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made by treating 2 grams of the phosphatic material without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, &c.) the residue insoluble in ammonium citrate is to be digested with HCl and $KClO_3$, as described below.

(5) *Total phosphoric acid.*—Weigh 2 grams into a flask or beaker, add 30 cubic centimeters concentrated hydrochloric acid, heat and add cautiously and in small quantities at a time about 0.5 gram finely-powdered potassium chlorate. Digest at a gentle heat until all phosphates are dissolved and all organic matter destroyed, dilute to 200 cubic centimeters; mix; pass through a dry filter; take 50 cubic centimeters of filtrate; neutralize with ammonia; for every decigram of P_2O_5 that is present, add 50 cubic centimeters of molybdic solution. Digest at about 65° C. for one hour filter and wash with ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution.) Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 cubic centimeters. Nearly neutralize with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (one drop per second), stirring vigorously. After 15 minutes add 30 cubic centimeters of ammonia solution of density 0.95. Let stand several hours (two hours is usually enough). Filter; wash with dilute ammonia; ignite intensely for 10 minutes and weigh.

(6) *Citrate-soluble phosphoric acid.* The sum of the water-soluble and citrate-insoluble subtracted from the total gives the citrate-soluble.

ANALYSIS OF NICKEL SPEISS.

Digest a weighed portion with strong HCl, at 60°–70° C., for some time, afterward bringing to a boil. Evaporate to dryness, take up with HCl + H_2O and filter. Or, complete solution may be obtained by digesting the sample in the above manner with Br and afterward taking up with HCl and H_2O. (This method of solution in Bromine is of *great value* with many Sulphides, especially where the S is to be estimated.)

Res. (*a*) = SiO_2.

Filt. (*a*). Heat to 70° C. Pass H_2S gas through the solution ½ hour, and filter.

Res. (*b*) = Sulphides of Cu, As, Sb etc.

Filt. (*b*). Boil. Oxidize H_2S with $KClO_3$, and expel excess of Cl by further boiling. Cool and precipitate Fe_2O_3 as basic acetate. Filter.

Res. (*c*) = Iron, etc.

Filt. (*c*). Concentrate to 200 c. c. Cool. Acidify with HCl and add water solution of freshly prepared Potassium xanthate. Filter, and wash thoroughly with water.

Res. (*d*) = Ni, Co, and Zn as xanthates.

Filt. (*d*). Contains Mn if present.

Wash *Res.* (*d*) on filter with dilute NH_4OH.

Res. (*e*) = Cobalt xanthate.

Dissolve this residue in strong HNO_3. Evaporate nearly to dryness, and add more HNO_3 + H_2SO_4 and evaporate again. The solution should be concentrated. Add $H_2C_2O_4$ + excess of C_2H_6O and boil, replacing the C_2H_6O as it evaporates. Filter *through sand* and wash with C_2H_6O. Wash the sand and Cobalt Oxalate into a flask and acidify with a few drops of H_2SO_4. The red color may be neutralized with a solution of Nickel Sulphate, after which titrate the oxalic acid with $\frac{N}{10}$ $KMnO_4$.

Filt. (*e*). Contains Nickel (and Zinc if present).

If Zn be present, the solution may be acidified with Citric Acid and treated with H_2S gas, when perfectly *cold*. If much Zn is present the gas should be passed at

intervals, for five minutes at a time, so as to avoid precipitation of Ni. Filter off ZnS and evaporate the filtrate to small bulk.

Evaporate almost to dryness with HNO_3 (conc.), and repeat with addition to H_2SO_4. To the concentrated solution add Oxalic Acid and further concentrate by boiling. Add excess of C_2H_6O and digest ½ hour, replacing the C_2H_6O. Filter as usual. Wash thoroughly with C_2H_6O and dissolve on filter with NH_4OH. Acidify with H_2SO_4, neutralize the green color with solution of Cobalt Sulphate and titrate the $H_2C_2O_4$ with $\frac{N}{10}$ $KMnO_4$. From the amount of $H_2C_2O_4$ calculate the Nickel.

REAGENTS.

Fusing Mixture.

2 parts $NaHCO_3$. 2 parts K_2CO_3. 1 part KNO_3. Pulverize very fine, and thoroughly mix, (or 2 parts anhydrous Na_2CO_3 and one part KNO_3). Test the mixtures for sulphur, and if present determine the amount.

Magnesia Mixture.

No. 1.	No. 2.
$MgCl_2$.....101.5 grms.	$MgSO_4$.....100. grms.
NH_4Cl.....200. "	NH_4Cl.....200. "
NH_4OH.....400. c. c.	NH_4OH.....400. c. c.
Water to make one litre.	Water.....800. "
1 c. c. = { 0.0355 grm. P_2O_5. / 0.0154 " P.	1 c. c. = (about) 0.01 grm. P.

Stannous Chloride.

50 grms. of the crystallized salt, dissolved in 500 c. c. of one-half strength HCl. This solution soon deteriorates, hence should not be made up in large quantities.

Mercuric Chloride.

A saturated solution; 60 grms. per litre.

Fused $KHSO_4$.

Heat some of the moist salt in a platinum dish or crucible to quiet fusion, and pour it on a porcelain slab. When cold, pulverize and place in a salt mouth bottle.

Molybdate Solution.

No. 1.

Take 3 grms. of ammonium molybdate, add 2 c. c. NH_4OH and triturate in a mortar; then add 20 c. c. of water (should dissolve); now pour this solution slowly into 20 c. c. of HNO_3 (1.20 sp. gr.), keeping it cold.

No. 2.

(*a*) Dissolve 100 grms. of MoO_3 in a mixture of 300 c. c. of strong NH_4OH and 100 c. c. of water.

(*b*) 1250 c. c. of HNO_3 (1.20 sp. gr.). Pour a little of (*b*) into (*a*), then all of (*a*) into (*b*) rapidly.

These solutions should stand several days before use.

Acid Solution Ammonium Nitrate.

Water.....	1 litre.
NH_4NO_3.....	100 grms.
HNO_3 (1.40 sp. gr.).....	15 c. c.

Purified Nitric Acid (1.40 sp. gr.)

Must be free from nitrous acid. If the bottle containing the acid has red fumes, blow air through the acid until the red fumes disappear, and then add 5 per cent. of water and place the bottle in a dark, cool place.

Nitric Acid (1.20 sp. gr.)

Add an equal volume of water to the 1.40 sp. gr. acid. It must be free from HCl and Cl.

Hydrochloric Acid.

Must be free from chlorine. If chlorine is present add strips of copper, let stand until it will not give a test for Cl, and then distil.

Tartaric Acid.

Tartaric Acid.....	40 grms.
Water.....	200 c. c.
Solution $BaCl_2$.....	10 c. c.

Boil the solution, then allow it to stand till the precipitate has completely subsided, and decant off the clear liquid for use.

Purified Asbestos.

Place a quantity of good, fibrous asbestos in a beaker, add some of the CrO_3 solution, then enough strong H_2SO_4 to thoroughly saturate, and heat for some time; pour the mass into a funnel and wash first with water acidulated with H_2SO_4, then with pure water, until the Cr_2O_3 and H_2SO_4 are removed; dry.

Oxide of Zinc Paste.

Fill a large sand or clay crucible with commercial oxide of zinc, cover and heat in a furnace at a bright red heat for some time, cool, and triturate with water to form a thin paste. It should not reduce $KMnO_4$.

Solution of Zinc Sulphate.

Dissolve 50 grms. of $ZnSO_4$ in water and dilute to 100 c. c.; add to this $KMnO_4$ solution until a faint pink color is produced; then add some oxide of zinc paste and shake thoroughly; allow it to subside, then filter or decant off the clear solution for use.

Dry, Granular Calcium Chloride Free From Calcium Oxide.

Take crystallized calcium chloride in a porcelain dish and heat very carefully (not above 200° C.) till fused, then stir constantly until granulated; now transfer the

dish to an air bath and heat at 200° C. till perfectly dry. Keep in well stoppered bottles. After filling the U-tubes pass dry CO_2 for one hour, then dry air until the CO_2 has been removed.

Double Chloride of Copper and Ammonium.

No. 1.

$CuCl_2, 2H_2O$	340 grms.
NH_4Cl	214 "
Water	1850 c. c.

When dissolved add enough NH_4OH to form a slight precipitate, allow this to subside and use only the clear solution. 50 c. c. of this solution will dissolve 1 grm. of steel or iron.

No. 2.

Make a saturated solution of the double chloride of copper and ammonium ($2NH_4Cl, CuCl_2 + 2H_2O$), add to it very dilute ammonia till a faint precipitate is produced, allow it to stand till the precipitate has subsided, then decant or filter off the clear solution.

Solution of CrO_3 and H_2SO_4.

Take 16 grms. CrO_3 and dissolve in 100 c. c. of water in a porcelain dish, add to this 260 c. c. of strong H_2SO_4. If on stirring, this fails to dissolve the precipitate which is first formed, add more H_2SO_4 till it is dissolved, then heat to incipient ebulliton. When cold it is ready for use. It should not be prepared long before-hand. 1 grm. of iron will require 30 c. c. of this solution. 90 c. c. will oxidize the carbon in 3 grms. of ordinary steel; the amount must be increased with the per cent. of carbon.

Anhydrous Copper Sulphate.

Take small pieces of pumice stone, soak them in a saturated solution of copper sulphate, and then heat them in an air bath for several hours at 250° C. Cool and keep in well stoppered bottles.

Standard Copper Sulphate.

Dissolve 3.95 grm. of pure $CuSO_4.5H_2O$ in water, add a few drops of H_2SO_4, and dilute to one litre. 1 c. c. will contain 0.001 grm. Cu.

Standard Potassium Cyanide.

Dissolve 5 grms. of Potassium Cyanide in 300 c. c. of water, and titrate it so that 1 c. c. will be equal to 1 c. c. of the copper solution.

Mode of titrating.—Take 5 c. c. of the standard copper solution, add NH_4OH till the precipitate first formed is dissolved and the solution is deep blue (avoid a large excess of NH_4OH); now run into it (cold) from a burette potassium cyanide until the blue color of the copper solution has disappeared. When the reaction is complete the solution will have a slight yellow tinge.

The cyanide solution loses strength by standing and must be compared often.

Standard Solution of Zinc Chloride.

Take 10 grms. Zn, dissolve in HCl, neutralize with NH_4OH, then add 15 c. c. HCl and 30 grms. NH_4Cl, and dilute to one litre.

Standard Potassium Ferrocyanide.

Take 43.2 grms. of the salt, dissolve in water and dilute to one litre. This should correspond volume for volume with the zinc solution; but the solutions should always be compared; for this purpose take 10 c. c. of the zinc solution, dilute to about 50 c. c., heat nearly to boiling, add a few drops of Uranium Acetate solution, then run in from a burette the Potassium Ferrocyanide solution, one-half c. c. at a time, shaking violently after each addition, until the precipitate appears flesh colored; or place a few drops of Uranium Acetate on a porcelain slab and add a drop of the solution with a glass rod, from time to time, till it gives a flesh color. While the

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zinc is in excess the precipitate is flocculent and subsides rapidly, but when the zinc is nearly all precipitated, the precipitate becomes fine and subsides very slowly, and a drop or two will produce the flesh color.

Potassium Xanthate.

Dissolve some caustic potash in absolute alcohol, filter if necessary, and add to the filtrate a large excess of carbon disulphide; a crystalline mass will soon form, which is brought on a filter and quickly washed with ether, and dried over sulphuric acid and paraffin. When dry, place in well corked bottles, and dissolve in water only the required amount when need for use, for the solution soon deteriorates.

Zinc Amalgam.

Place a quantity of granulated zinc in a dish, cover with mercury, and add a very dilute solution of sulphuric acid, and stir till action ceases; then place in a funnel to drain off the excess of mercury.

Battery Solution.

For a Bunsen element. For the porous cell use a saturated solution of $K_2Cr_2O_7$ to which has been added one-fifth its volume of H_2SO_4. For the outer cell use a solution of 1 part H_2SO_4. For the outer cell use a solution of 1 part H_2SO_4 and nine parts water.